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PATENT & TRADEMARK OFFICE

Attorney Docket No. 56702 (70801)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Nobuyuki Takamori, *et al.*

Application No.: 10/002,949 — Confirmation No.: 5456

Filed: November 15, 2001 — Art Unit: 1756

For: OPTICAL DATA RECORDING MEDIUM — Examiner: M. J. Angebranndt

Mail Stop Appeal Brief—Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

BRIEF ON APPEAL

Sir:

This Appeal Brief was originally filed on December 4, 2006, and is being resubmitted with a revised "Argument" section, as required in the Office communication mailed on March 9, 2007. A request for an extension of time accompanies this Appeal Brief.

This is an appeal from the final rejection of claims 10-22, as included in the Final Office Action mailed by the U.S. Patent and Trademark Office on February 2, 2006.

BRIEF ON APPEAL FEE

Authorization to charge Deposit Account No. 04-1105 for $500.00, covering the appeal brief fee, was provided previously. However, if for any reason a fee is required, a fee paid is inadequate or credit is owed for any excess fee paid, the Commissioner is hereby authorized and requested to charge Deposit Account No. **04-1105**.

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REAL PARTY IN INTEREST

The real party in interest is Sharp Kabushiki Kaisha. The assignment of the inventors to this corporation was recorded on November 15, 2001, at Reel 012355, Frame 0205.

RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences known to Appellants, Appellants' legal representative, or the assignee which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal. However, certain related issues were raised by the appeal filed in co-owned application serial no. 10/002,952.

STATUS OF CLAIMS

Claims 1-22 have been presented in this application. Claims 1-9 have been cancelled. Claims 10-22 stand finally rejected. Claims 10-22 are appealed. See the Claims Appendix attached hereto.

STATUS OF AMENDMENTS

No amendments were filed after final rejection.

A clean set of the claims on appeal is set forth in the Claims Appendix hereto.

SUMMARY OF CLAIMED SUBJECT MATTER

Independent claims 10, 14 and 18 are pending in the application.

The present invention provides optical data recording medium which are resistant to deformation (e.g., warp) due to changes in temperature. More particularly, the present invention provides optical data recording media in which the expansion coefficient of the protective film and the transparent substrate are regulated to prevent a bending force that can induce a warp or bend in the medium (see, e.g., page 6, lines 10-13). The present inventors have discovered that selecting the materials used in the protective layer and the transparent substrate provides superior thermal stability and reduced medium deformation.

Independent claim 10 recites an optical data recording medium comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein the thin film layer is a single layered or multilayered film including at least any one of a dielectric film, a recording film and a reflective film (see, e.g., page 6, lines 14-21). In claim 10, at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate, and the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) (see, e.g., page 21, lines 10-18, and Figure 5) and smaller than 5.0×10^{-4} (1/°C), and an expansion coefficient under humidity of the protective film is 1.7×10^{-4}(1/%) or smaller (see, e.g., page 27, lines 18-19).

Independent claim 14 recites an optical data recording medium, comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein a Young's modulus of the transparent substrate is smaller than 10.0×10^{9}(Pa), and the thin film layer is a single layered or multilayered film. In claim 14, at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate, and the linear expansion coefficient of

the protective film is greater than 9.5×10^{-5} (l/°C) and smaller than 5.0×10^{-4} (1/°C), and an expansion coefficient under humidity of the protective film is 1.7×10^{-4}(1/%) or smaller (see, e.g., page 27, lines 18-19).

Independent claim 18 recites a method of selecting a protective film in an optical data recording medium, the optical data recording medium comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein the transparent substrate has a Young's modulus smaller than 10.0×10^{9}(Pa), and wherein the thin film layer is a single layered or multilayered film including at least any one of a dielectric film, a recording film and a reflective film and the transparent substrate is made of a polycarbonate or a polyolefin with a thickness of 0.5 mm. The method includes the steps of:

determining the linear expansion coefficient of a material for making the protective film; and

selecting the material for making the protective film such that at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate and the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C) (see, e.g., page 27, lines 18-19, and original claims 7 and 8).

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The grounds of rejection to be reviewed on appeal are:

(1) Whether claims 10-16 are unpatentable under 35 USC §102(b) over U.S. Patent No. 5,714,222 to Yokoyama et al. (hereinafter "Yokoyama").

(2) Whether claims 10-16 are unpatentable under 35 USC §102(b) over U.S. Patent No. 5,674,649 to Yoshioka et al. (hereinafter "Yoshioka").

(3) Whether claims 10-16 are unpatentable under 35 USC §102(b) over U.S. Patent No. 5,102,709 to Tachibana et al. (hereinafter "Tachibana").

(4) Whether claims 10-17 and 22 are unpatentable under 35 USC §103(a) over Tachibana.

(5) Whether claims 10-22 are unpatentable under 35 USC §103(a) over EP1031972 to Tajima et al. (hereinafter "Tajima").

ARGUMENT

1. Brief summary of argument

Three Section 102(b) rejections and two Section 103(a) rejections are outstanding in this case. The rejections cannot be sustained.

The cited documents do not disclose or otherwise suggest (explicitly or inherently) Appellant's claimed invention. In particular, the documents do not disclose optical recording media according to the pending claims, in which either one of a linear expansion coefficient and a Young's modulus of a protective film is greater than that of a transparent substrate, and the linear expansion coefficient of the protective film has a predetermined value.

The rejected claims do *not* stand or fall together since certain claims are considered separately patentable. Appellant submits that all of the claims under appeal are patentable including for reasons set forth below.

2. Examiner's position

The Examiner has stated that each of the Yokoyama, Yoshioka, Tachibana and Tajima references describes all the features of certain of the pending claims and/or renders obvious the pending claims. The Examiner concedes that the references do not explicitly describe optical media having the claimed properties, but the Examiner has taken the position that the references inherently disclose optical recording media having the properties of Appellant's claimed media.

For example, the Examiner states that "the position of the examiner is that the resins of the prior art inherently have the recited properties and is congruent with the specification of the applicant." See page 4 of the Final Office Action dated February 2, 2006.

3. Appellant's arguments

A. Claims 10-16 are not unpatentable under 35 USC §102(b) over U.S. Patent No. 5,714,222 to Yokoyama et al.

i. The Yokoyama reference does not disclose all the features of the claimed invention, explicitly or inherently.

The Yokoyama reference is directed to optical recording media having a protective layer or layers over a recording layer. According to Yokoyama, the protective layer is formed by spin-coating the protective layer over the substrate (see, e.g., the Abstract). The protective layer may be formed from epoxyacrylate resins or urethane acrylate resins. Yokoyama does not describe the expansion properties of any layer of the recited overcoating and more particularly does not teach or suggest controlling the warp or tilt of the optical recording media by modulating the linear expansion coefficient of one or more of the layers constituting the optical recording media.

ii. The Yokoyama reference neither anticipates nor renders obvious the pending claims.

Claims 10-16 stand rejected over the Yokoyama reference, the teachings of which are described above. The rejection is traversed.

It is well-established that a claim is anticipated only if each and every element or feature of a claim is expressly or inherently described in a single prior art reference. See, e.g., MPEP 2131.

In the present case, the Examiner appears to agree that the Yokoyama reference does not expressly disclose all the elements of the presently-claimed invention. The Examiner nevertheless rejected the claims because "[t]he position of the Examiner is that the resins of the prior art inherently have the recited properties." Final Office Action at page 4.

Inherency, however, may not be established by probabilities or possibilities." MPEP 2112(IV), citing *In re Robertson*, 169 F.3d 743, 745 (Fed. Cir. 1999) (citations omitted) (emphasis added).

The Examiner further states that "applicant argues that various polycarbonates are known and that the polycarbonates used by Yokoyama '222 are necessarily similar enough to those of the instant specification to have the recited properties." Appellants believe that this statement should read " . . . the polycarbonates used by Yokoyama '222 are not necessarily similar enough to those of the instant specification to have the recited properties;" the statement as originally quoted is not Appellants' position at all. Indeed, Appellants do consider that the materials disclosed by Yokoyama do not necessarily have the properties recited in the present claims, and therefore cannot anticipate the pending claims.

The Examiner also states that "urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims in the instant specification…" Final Office Action at page 3.

The Examiner appears to take the position that all urethane, epoxy, polyester and polyether acrylates which can be used in optical recording media inherently possess linear expansion coefficient and/or expansion coefficient under humidity and/or Young's modulus values specified in the pending claims.

Appellants respectfully contend that a mere assertion that a property is inherent is insufficient to prove that a reference is anticipatory. Although Appellants agree that certain urethane, epoxy, polyester or polyether acrylate materials are useful in the present invention, the

pending claims further require that each material used in the protective layer or the transparent substrate possess specified values for the properties recited in the pending claims. Thus, the instant invention contemplates fabrication of the transparent substrate and protective layer from materials such as urethane, epoxy, polyester or polyether acrylate materials (or polyolefin or polycarbonate) which possess the requisite linear expansion coefficient and Young's modulus (e.g., as specified in independent claim 10 and claims dependent therefrom) or linear expansion coefficient, Young's modulus, and expansion coefficient under humidity (e.g., as specified in independent claim 14 and the claims dependent therefrom). While the Examiner states that "urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims," Appellants contend that the instant specification does not suggest that all polyester, epoxy, urethane or polyether acrylates are useful in the present invention. Rather, the present specification teaches that those materials meeting *specified limitations* of linear expansion coefficient, Young's modulus, and/or expansion coefficient under humidity, are useful in the claimed invention.

The claimed invention of claims 10-14 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C). The claimed invention of claims 14-16 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C) and an expansion coefficient under humidity of the protective film is 1.70×10^{-4} (1/%) or smaller. As disclosed by the present specification, optical data recording media which satisfy the above requirements are particularly resistant to deformation or warpage.

For a reference to inherently disclose a feature not expressly disclosed, extrinsic evidence can be used to supply the missing feature if the extrinsic evidence "make[s] clear that the missing descriptive matter is *necessarily present* in the thing described in the reference and that it would be so recognized by persons of ordinary skill in the art. However, the Examiner has not provided

any extrinsic evidence that Yokoyama discloses *all the features* of the claimed invention.

The Yokoyama reference does not disclose materials having the characteristics of the claimed optical recording medium. Moreover, no extrinsic evidence has been presented to show or establish that the protective layers or transparent substrates of the optical recording media of Yokoyama necessarily possess the characteristics recited in claims 10 and 14 (and the claims dependent thereupon).

Appellants respectfully submit that the materials disclosed in the Yokoyama reference do not necessarily possess the properties of the claimed invention. Materials described in similar general terms can and often do have quite different properties, including different linear expansion coefficient, Young's modulus and/or expansion coefficient under humidity. It is clear that a reference disclosing a urethane acrylate, epoxy acrylate, or polyester or polyether acrylate would not necessarily provide a disclosure of a material having the claimed expansion coefficient under humidity.

B. Claims 10-16 are not unpatentable under 35 USC §102(b) over U.S. Patent No. 5,674,649 to Yoshioka et al.

i. The Yoshioka reference does not disclose all the features of the claimed invention, explicitly or inherently.

The Yoshioka reference is directed to optical recording media having a recording layer which becomes amorphous with increased temperature and then melts and quenches by absorbing laser energy (see, e.g., Col. 2, lines 21-35). According to Yoshioka, the optical recording medium optionally includes an "overcoat protective layer" (see, e.g., Col. 2, lines 50-52).

Yoshioka does not describe the expansion properties of any layer of the recited overcoating and more particularly does not teach or suggest controlling the warp or tilt of the optical recording media by modulating the linear expansion coefficient of one or more of the layers constituting the optical recording media. The Yoshioka reference does not expressly disclose any linear expansion coefficient for the protective coatings therein.

ii. The Yoshioka reference neither anticipates nor renders obvious the pending claims.

Claims 10-16 stand rejected over the Yoshioka reference, the teachings of which are described above. The rejection is traversed.

It is well-established that a claim is anticipated only if each and every element or feature of a claim is expressly or inherently described in a single prior art reference. See, e.g., MPEP 2131.

In the present case, the Examiner appears to agree that the Yoshioka reference does not expressly disclose all the elements of the presently-claimed invention. The Examiner refers to Yoshioka as disclosing an optical recording medium "coated with a UV cured urethane-acrylate." Final Office Action at page 5. The Examiner rejected the claims over Yoshioka "for the reasons provided above [with respect to Yokoyama]." Final Office Action at page 5.

This rejection fails for at least the reason described above. As with the Yokoyama reference, the Examiner also states that "urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims in the instant specification…" Final Office Action at page 5.

The Examiner appears to take the position that all urethane, epoxy, polyester and polyether acrylates which can be used in optical recording media inherently possess linear expansion coefficient and/or expansion coefficient under humidity and/or Young's modulus values specified in the pending claims.

Appellants respectfully contend that a mere assertion that a property is inherent is insufficient to prove that a reference is anticipatory. While the Examiner states that "urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims," Appellants contend that the instant specification does not suggest that all polyester, epoxy, urethane or polyether acrylates are useful in the present invention. Rather, the present specification teaches that those materials meeting *specified limitations* of linear expansion coefficient, Young's modulus, and/or expansion coefficient under humidity, are useful

in the claimed invention.

The claimed invention of claims 10-14 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C). The claimed invention of claims 14-16 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C) and an expansion coefficient under humidity of the protective film is 1.70×10^{-4} (1/%) or smaller. As disclosed by the present specification, optical data recording media which satisfy the above requirements are particularly resistant to deformation or warpage.

For a reference to inherently disclose a feature not expressly disclosed, extrinsic evidence can be used to supply the missing feature if the extrinsic evidence "make[s] clear that the missing descriptive matter is *necessarily present* in the thing described in the reference and that it would be so recognized by persons of ordinary skill in the art. However, the Examiner has not provided any extrinsic evidence that Yoshioka discloses *all the features* of the claimed invention.

The Yoshioka reference does not disclose materials having the characteristics of the claimed optical recording medium. Moreover, no extrinsic evidence has been presented to show or establish that the protective layers or transparent substrates of the optical recording media of Yoshioka necessarily possess the characteristics recited in claims 10 and 14 (and the claims dependent thereupon).

Appellants respectfully submit that the materials disclosed in the Yoshioka reference do not necessarily possess the properties of the claimed invention. Materials described in similar general terms can and often do have quite different properties, including different linear expansion coefficient, Young's modulus and/or expansion coefficient under humidity. It is clear that a reference disclosing a urethane acrylate, epoxy acrylate, or polyester or polyether acrylate would not necessarily provide a disclosure of a material having the claimed expansion coefficient under humidity.

C. Claims 10-16 are not unpatentable under 35 USC §102(b) over U.S. Patent No. 5,102,709 to Tachibana et al.

i. The Tachibana reference does not disclose all the features of the claimed invention, explicitly or inherently.

The Tachibana reference is directed to optical recording media having a protective layer (see, e.g., Col. 2, lines 20-29). According to Tachibana, the protective layer or "resinous protective layer" can include a cured film of a photocurable resin including a polyfunctional acrylate compound and/or a urethane acrylate compound (see, e.g., Col. 2, lines 30-40). Tachibana does not describe the expansion properties of any layer of the recited overcoating and more particularly does not teach or suggest controlling the warp or tilt of the optical recording media by modulating the linear expansion coefficient of one or more of the layers constituting the optical recording media. The Tachibana reference does not expressly disclose any linear expansion coefficient for the protective coatings therein.

ii. The Tachibana reference neither anticipates nor renders obvious the pending claims.

Claims 10-16 stand rejected over the Tachibana reference, the teachings of which are discussed above. The rejection is traversed.

It is well-established that a claim is anticipated only if each and every element or feature of a claim is expressly or inherently described in a single prior art reference. See, e.g., MPEP 2131.

In the present case, the Examiner appears to agree that the Tachibana reference does not expressly disclose all the elements of the presently-claimed invention. The Examiner refers to Tachibana as disclosing an optical recording medium "coated with a UV cured urethane-acrylate . . . ." Final Office Action at page 5. The Examiner rejected the claims over Tachibana "for the reasons provided above [with respect to Tachibana]." Final Office Action at page 5.

This rejection fails for at least the reason described above. As with the Yokoyama and Yoshioka references, the Examiner also states that "urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims in the instant specification..." Final Office Action at page 6.

The Examiner appears to take the position that all urethane, epoxy, polyester and polyether acrylates which can be used in optical recording media inherently possess linear expansion coefficient and/or expansion coefficient under humidity and/or Young's modulus values specified in the pending claims.

Appellants respectfully contend that a mere assertion that a property is inherent is insufficient to prove that a reference is anticipatory. While the Examiner states that "urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims," Appellants contend that the instant specification does not suggest that all polyester, epoxy, urethane or polyether acrylates are useful in the present invention. Rather, the present specification teaches that those materials meeting *specified limitations* of linear expansion coefficient, Young's modulus, and/or expansion coefficient under humidity, are useful in the claimed invention.

The claimed invention of claims 10-14 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C). The claimed invention of claims 14-16 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C) and an expansion coefficient under humidity of the protective film is 1.70×10^{-4} (1/%) or smaller. As disclosed by the present specification, optical data recording media which satisfy the above requirements are particularly resistant to deformation or warpage.

For a reference to inherently disclose a feature not expressly disclosed, extrinsic evidence can be used to supply the missing feature if the extrinsic evidence "make[s] clear that the missing

descriptive matter is *necessarily present* in the thing described in the reference and that it would be so recognized by persons of ordinary skill in the art. However, the Examiner has not provided any extrinsic evidence that Tachibana discloses *all the features* of the claimed invention.

The Tachibana reference does not disclose materials having the characteristics of the claimed optical recording medium. Moreover, no extrinsic evidence has been presented to show or establish that the protective layers or transparent substrates of the optical recording media of Tachibana necessarily possess the characteristics recited in claims 10 and 14 (and the claims dependent thereupon).

Appellants respectfully submit that the materials disclosed in the Tachibana reference do not necessarily possess the properties of the claimed invention. Materials described in similar general terms can and often do have quite different properties, including different linear expansion coefficient, Young's modulus and/or expansion coefficient under humidity. It is clear that a reference disclosing a urethane acrylate, epoxy acrylate, or polyester or polyether acrylate would not necessarily provide a disclosure of a material having the claimed expansion coefficient under humidity.

Like the references discussed above, the Tachibana reference does not expressly disclose *any* linear expansion coefficient for the protective coatings therein, let alone a linear expansion coefficient of the protective film in the range recited in the present claims, and there is no teaching that the materials necessarily possess all the properties recited in the pending claims.

Moreover, although the Examiner states that the Tachibana reference discloses that certain media have a certain warpage after durability testing, the warpage data disclosed in the Tachibana patent do not demonstrate that the optical recording media there disclosed meet the limitations of the present claims. The warp of exhibited by a particular recording medium is the result of a variety of factors, and the Examiner has not demonstrated that the observed warpage results of Tachibana are the result of, e.g., the substrate and protective film of Tachibana meeting the limitations of the present claims.

D. Claims 10-17 and 22 are not unpatentable under 35 USC §103(a) over U.S. Patent No. 5,102,709 to Tachibana et al.

Claims 10-17 and 22 stand rejected under 35 USC §103(a) over the Tachibana reference. The rejection is traversed.

The teachings of the Tachibana reference, and the differences between Tachibana and independent claims 10 and 14, have been discussed above. Appellants contend that claims 10 and 14, and the claims dependent therefrom, are not obvious in view of Tachibana for at least the reasons discussed above. As discussed above, Appellants contend that Tachibana does not disclose media having the specified properties of the pending claims. In view of the *silence* of Tachibana as to these properties, Appellants respectfully urge that it would not have been obvious to one of ordinary skill to modify the teachings of Tachibana to arrive at the claimed invention. Tachibana cannot teach or suggest materials having properties that Tachibana does not even describe. Because Tachibana does not expressly disclose the properties of the materials as recited in the pending claims, there could not be any motivation to modify the teachings of Tachibana as suggested by the Examiner to arrive at the claimed invention.

Moreover, the invention of claim 22 is directed to an optical data recording medium provided with a protective film for protecting a thin film layer selected by the method of any one of claims 18 to 21. The methods of claims 18-21 include the steps of determining the linear expansion coefficient of a material for making the protective film; and selecting the material for making the protective film such that at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate and the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C). The Examiner has not even asserted that Tachibana anticipates or renders obvious any of claims 18 to 21 (as indeed it does not). Tachibana does not disclose or render obvious a method as recited in any of claims 18-21. Appellants submit that claim 22, which is directed to an optical data recording medium provided with a protective film for protecting a thin film layer selected by such a method, cannot be rendered obvious by Tachibana, in view of Tachibana's lack of disclosure of optical data recording media having the

recited properties, the importance of the recited properties, or methods for selecting materials having desirable properties for use in such optical data recording media. Tachibana does not and cannot render obvious the pending claims.

E. Claims 10-22 are not unpatentable under 35 USC §103(a) over EP1031972 to Tajima et al.

i. The Tajima reference does not disclose all the features of the claimed invention, explicitly or inherently.

The Tajima reference is directed to optical recording media in which the warpage caused by temperature changes is reduced (see, e.g., the Abstract).

At paragraphs [0035]-[0041], the Tajima reference discloses an example of an optical information recording medium made of three layers (a transparent substrate, a thin film layer, and a thin film protective coating). In this medium, the linear expansion coefficients and thicknesses of the transparent substrate and the thin film protective coat are adjusted to reduce the warp of the medium caused by temperature change.

ii. The Tajima reference does not render obvious the pending claims.

Claims 10-22 stand rejected over the Tajima reference under 35 USC §103(a). The rejection is traversed.

The Examiner describes the Tajima reference as disclosing "optimization of linear expansion coefficient, thickness and Young's modulus of the protective layer to offset the stresses on either side of the dielectric layer due to the substrate to reduce warpage," Final Office Action at page 7, but the Examiner apparently agrees that Tajima does not disclose materials having the linear expansion coefficients recited in the pending claims. However, the Examiner states that "[I]t would have been obvious to one skilled in the art to modify the example [of Tajima] by doubling the linear expansion coefficient . . . and decreasing the

thickness nearly by half to . . . maintain the same force on the side of the medium opposite the side of the substrate." Final Office Action at page 7. Appellants cannot agree with these statements.

The Examiner also states that "the examiner holds that the last layer to be coated/formed would be the obvious choice for optimization . . . by choosing resins compositions which have higher linear expansion coefficients." Final Office Action at p. 8.

However, as the Examiner seems to acknowledge, the linear coefficient of expansion of the protective film of the present invention is different from, and greater than, the linear expansion coefficient disclosed in Tajima (EP1031972) (see, e.g., Table 1 of Tajima).

The claimed invention of claims 10-14 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C).

The claimed invention of claims 14-16 provides that the material of the protective film has at least one of a linear expansion coefficient and a Young's modulus value greater than that of the transparent substrate and that the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C) and an expansion coefficient under humidity of the protective film is 1.70×10^{-4} (1/%) or smaller. As disclosed by the present specification, optical data recording media which satisfy the above requirements are particularly resistant to deformation or warpage.

Claim 18 (and the claims dependent therefrom) is directed to a method of selecting a protective film in an optical data recording medium, the optical data recording medium comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein the transparent substrate has a Young's modulus smaller than 10.0×10^{9}(Pa), and wherein the thin film layer is a single layered or multilayered film including at least any one of a dielectric film, a recording film and a reflective film and the transparent substrate is made of a polycarbonate or a polyolefin with a

thickness of 0.5 mm. The method includes the steps of: determining the linear expansion coefficient of a material for making the protective film; and selecting the material for making the protective film such that at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate and the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C).

Appellants respectfully contend that the Examiner's proposed modification of the Tajima reference appears to rely on hindsight; that is, the Examiner's view of the Tajima reference is colored by the teachings of the instant specification. The Examiner appears to be using the teachings of the present invention as a road-map to modify the teachings of the prior art to thereby arrive at the presently-claimed invention. This is an improper hindsight rejection; see, e.g., *Grain Processing Corp. v. American Maize-Prods. Co.*, 840 F.2d 902, 907, 5 USPQ2d 1788, 1792 (Fed. Cir. 1988). Appellants respectfully contend that, prior to the present invention, one of ordinary skill in the art would not have been motivated to make the modifications suggested by the Examiner.

Moreover, one of ordinary skill in the art would not have had a reasonable expectation of success in making the modification to the teachings of Tajima as suggested by the Examiner. The Examiner has not pointed to any teaching in Tajima (or anywhere else) of materials having all the properties (and relationships among properties of the various components) recited in the pending claims. Prior to the present invention, one of ordinary skill in the art would not have had a reasonable expectation of success in making the modification to the teachings of Tajima as suggested by the Examiner. For this reason, too, the claims are not obvious in view of Tajima.

F. Comparative data effectively rebuts any *prima facie* case of anticipation or obviousness that may be contended to exist

Moreover, while Appellant fully believes that a *prima facie* case of anticipation under 35 U.S.C. 102(b) or obviousness under 35 U.S.C. 103(a) has not been made by the Examiner, it is

also believed that previously-presented test data fully rebuts any *prima facie* case that may be contended to exist.

As Appellants pointed out in the "Preliminary Amendment (Filed With Request for Continued Examination)" filed on March 22, 2005 (a copy of the pertinent part of which is attached hereto as Exhibit E), materials described in similar general terms can and often do have quite different properties, including different linear expansion coefficients. For example, as shown on the attached Table (also reproduced at Exhibit E), materials generically termed "acrylic UV curable resins" having similar principal components can nevertheless have a range of linear expansion coefficients (in the Table, ranging from about 1.10×10^{-5} to about 1.46×10^{-4} (1/°C) (note that the acrylic ester commercial product listed at the bottom of the Table does not have a linear expansion coefficient within the range required by the instant claims). It is clear that a reference disclosing an acrylic UV curable resin would not <u>necessarily</u> provide a disclosure of an acrylic UV curable resin having a linear expansion coefficient *in a specific range*.

The Examiner has suggested that "direct comparison with the prior art" could obviate the rejections of record. Appellants note that certain resins disclosed in the cited references are apparently no longer produced. For example, Appellants also note that, contrary to the Examiner's suggestion that the resin "SD101 appears to be still available," Final Office Action at page 5, it is believed that this material is no longer sold.

In the "Response to Non-final Office Action" dated January 26, 2006 (a copy of the pertinent part of which is attached hereto at Exhibit F), Appellants provided the following data and remarks:

The resin composition disclosed in Example 3 of Tachibana (KAYARAD DPCA-30 (70%), KAYARAD R-604 (25%), IRG-184, 5%) has a linear expansion coefficient of 9.0×10^{-5} (1/°C). This linear expansion coefficient is not within the range of values of the linear expansion coefficient recited by the pending claims (greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4}(1/°C)). Thus, this composition does not in fact possess the properties of the claimed invention, and cannot anticipate the pending claims. There is no teaching or suggestion in

Tachibana that this resin or any other materials disclosed therein necessarily possess all the properties recited in the pending claims.

Appellants contend that this experiment provides additional support for Appellants' contention that the cited references do not necessarily disclose materials for optical data recording media having the properties of the claimed media. Appellants therefore contend that the inherency rejection cannot be maintained.

In the Final Office Action, the Examiner stated that "there is no basis for why this [data] could possibly be a better comparison than one with the cited example." Final Office Action at page 6. However, the data described above establish that the Examiner's primary premise – that "[in the cited references] urethane, epoxy, polyester and polyether acrylates are disclosed as useful and meeting the material limitation of the claims" – is flawed, and that the cited references (not only Tachibana) therefore cannot inherently disclose materials meeting the limitations of the pending claims. Appellants have provided counter-examples which demonstrate that the Examiner's position on inherency is unsound. See, e.g., MPEP 2112(V).

In summary, the cited references do not teach or suggest optical recording media of the present claims which are resistant to deformation or warpage. None of the references teaches or suggests that the materials used in the fabrication of the optical recording media should be selected to have the claimed properties.

G. The remaining claims on appeal are separately patentable

The cited references also provide no disclosure of other aspects of Appellant's claimed invention.

a) Claim 11

Claim 11 is separately patentable for the above-stated reasons and further because the cited references fail to teach or suggest the optical recording medium of claim 10 wherein an expansion coefficient under humidity (ratio of expansion (1/%) where a difference of relative humidity (vapor content/ saturated vapor amount at 25°C) is increased by 1%) of the

protective film is 1.7×10^{-4}(1/%) or smaller. The cited references do not teach or suggest this feature of claim 11.

b) Claims 12 and 13

Claims 12 and 13 are separately patentable for the above-stated reasons and further because the cited references fail to teach or suggest the optical recording medium of claim 10 (or 11) wherein the Young's modulus of the transparent substrate is smaller than 10.0×10^{9}(Pa). The cited references do not teach or suggest this feature of claims 12 and 13.

c) Claim 19

Claim 19 is separately patentable for the above-stated reasons and further because the cited references fail to teach or suggest the method of selecting a protective film in an optical data recording medium according to claim 18 wherein the protective film is selected such that the Young's modulus of the protective film is greater than 2.0×10^{9}(Pa) and smaller than 1.0×10^{10}(Pa). The cited references do not teach or suggest this feature of claim 19.

c) Claims 20 and 21

Claims 20 and 21 are separately patentable for the above-stated reasons and further because the cited references fail to teach or suggest the method of selecting a protective film in an optical data recording medium according to claim 18 (or 19) wherein the protective film is selected such that an expansion coefficient under humidity thereof (ratio of expansion (1/%) where a difference of relative humidity (vapor content/saturated vapor amount at 25°C) is increased by 1%) of the protective film is 1.7×10^{-4}(1/%) or smaller. The cited references do not teach or suggest this feature of claims 20 and 21.

SUMMARY

Appellants submit that all of the claims under final rejection are in condition for allowance and should be allowed, and that the Final Office Action should be vacated.

If for any reason a fee is required, a fee paid is inadequate or credit is owed for any excess fee paid, you are hereby authorized and requested to charge Deposit Account No. **04-1105**, under Reference No. 56702 (70801), Customer No. 21874.

Respectfully submitted,

Date: May 9, 2007

By: ______________________

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CLAIMS APPENDIX

1-9. (Cancelled).

10. An optical data recording medium comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein the thin film layer is a single layered or multilayered film including at least any one of a dielectric film, a recording film and a reflective film, and at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate, and the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4}(1/°C).

11. An optical data recording medium according to claim 10, wherein an expansion coefficient under humidity (ratio of expansion (1/%) where a difference of relative humidity (vapor content/ saturated vapor amount at 25°C) is increased by 1%) of the protective film is 1.7×10^{-4}(1/%) or smaller.

12. An optical data recording medium according to claim 10, wherein the Young's modulus of the transparent substrate is smaller than 10.0×10^{9}(Pa).

13. An optical data recording medium according to claim 11, wherein the Young's modulus of the transparent substrate is smaller than 10.0×10^{9}(Pa).

14. An optical data recording medium, comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein a Young's modulus of the transparent substrate is smaller than 10.0×10^{9}(Pa), and the thin film layer is a single layered or multilayered film, and wherein at least either one of a linear expansion

coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate, and the linear expansion coefficient of the protective film is greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C), and an expansion coefficient under humidity of the protective film is 1.7×10^{-4}(1/%) or smaller.

15. An optical data recording medium according to any one of claims 10 to 14, wherein a thickness of the protective film is 5 μm or more to 20 μm or less.

16. An optical data recording medium according to any one of claims 10 to 14, wherein the protective film is made of an ultraviolet light curing resin.

17. An optical data recording medium according to any one of claims 10 to 14, wherein the transparent substrate is made of a polycarbonate or a polyolefin and a thickness thereof is about 0.5 mm.

18. A method of selecting a protective film in an optical data recording medium, the optical data recording medium comprising a transparent substrate, a thin film layer formed on the transparent substrate and a protective film which is mainly comprised of a resin and formed on the thin film layer for protecting the thin film layer, wherein the transparent substrate has a Young's modulus smaller than 10.0×10^{9}(Pa), and wherein the thin film layer is a single layered or multilayered film including at least any one of a dielectric film, a recording film and a reflective film and the transparent substrate is made of a polycarbonate or a polyolefin with a thickness of 0.5 mm, the method comprising the steps of:

determining the linear expansion coefficient of a material for making the protective film; and

selecting the material for making the protective film such that at least either one of a linear expansion coefficient and a Young's modulus of the protective film is greater than that of the transparent substrate and the linear expansion coefficient of the protective film is

greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4} (1/°C).

19. A method of selecting a protective film in an optical data recording medium according to claim 18, wherein the protective film is selected such that the Young's modulus of the protective film is greater than 2.0×10^{9}(Pa) and smaller than 1.0×10^{10}(Pa).

20. A method of selecting a protective film in an optical data recording medium according to claim 18, wherein the protective film is selected such that an expansion coefficient under humidity thereof (ratio of expansion (1/%) where a difference of relative humidity (vapor content/saturated vapor amount at 25°C) is increased by 1%) of the protective film is 1.7×10^{-4}(1/%) or smaller.

21. A method of selecting a protective film in an optical data recording medium according to claim 19, wherein the protective film is selected such that an expansion coefficient under humidity thereof (ratio of expansion (1/%) where a difference of relative humidity (vapor content/saturated vapor amount at 25°C) is increased by 1%) of the protective film is 1.7×10^{-4}(1/%) or smaller.

22. An optical data recording medium provided with a protective film for protecting a thin film layer selected by the method of any one of claims 18 to 21.

EVIDENCE APPENDIX

Tab A	Copy of U.S. Patent No. 5,714,222 to Yokoyama et al. ("Yokoyama"), as relied on by the Examiner in the Final Office Action of 02/02/2006.
Tab B	Copy of U.S. Patent No. 5,674,649 to Yoshioka et al.("Yoshioka "), as relied on by the Examiner in the Final Office Action of 02/02/2006.
Tab C	Copy of U.S. Patent No. 5,102,709 to Tachibana et al. ("Tachibana "), as relied on by the Examiner in the Final Office Action of 02/02/2006.
Tab D	Copy of EP 1031972 to Tajima et al. ("Tajima "), as relied on by the Examiner in the Final Office Action of 02/02/2006.
Tab E	Portion of "Preliminary Amendment (Filed With Request for Continued Examination)" as filed by Appellants, dated March 22, 2005.
Tab F	Portion of "Response to Non-final Office Action" as filed by Appellants, dated January 26, 2006.

RELATED PROCEEDINGS APPENDIX

None.

Appendix A

US005714222A

United States Patent [19]
Yokoyama

[11] Patent Number: 5,714,222
[45] Date of Patent: Feb. 3, 1998

[54] **OPTICAL RECORDING MEDIUM AND PROCESS FOR PRODUCING SAME**

[75] Inventor: **Ryuichi Yokoyama**, Yokohama, Japan

[73] Assignee: **Canon Kabushiki Kaisha**, Tokyo, Japan

[21] Appl. No.: **588,815**

[22] Filed: **Jan. 19, 1996**

[30] **Foreign Application Priority Data**

Jan. 23, 1995 [JP] Japan 7-008010

[51] **Int. Cl.**[6] **B32B 3/00**

[52] **U.S. Cl.** **428/64.1**; 428/64.2; 428/64.3; 428/64.4; 428/64.7; 428/913; 430/270.11; 430/495.1; 430/945; 369/283; 369/288; 427/372.2; 427/385.5

[58] **Field of Search** 428/64.1, 64.2, 428/64.4, 64.3, 64.7, 913; 430/270.1, 270.11, 495.1, 945; 369/283, 288; 427/372.2, 385.5

[56] **References Cited**

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Primary Examiner—Patrick Ryan
Assistant Examiner—Elizabeth Evans
Attorney, Agent, or Firm—Fitzpatrick, Cella, Harper & Scinto

[57] **ABSTRACT**

The optical recording medium has an optically transparent substrate having a center hole, a recording layer formed on the substrate, and a protective layer. The protective layer has an opening whose center coincides with a center of the center hole of the substrate, and the opening of the protective layer is larger than the center hole of the substrate. The optical recording medium is produced by a process including the steps of forming the protective layer for covering the recording layer so that the protective layer has an opening whose center coincides with a center of the center hole, and forming the opening of the protective layer so that it is larger than the center hole of the substrate. The step of forming the protective layer may be achieved using a spin coating method.

22 Claims, 1 Drawing Sheet

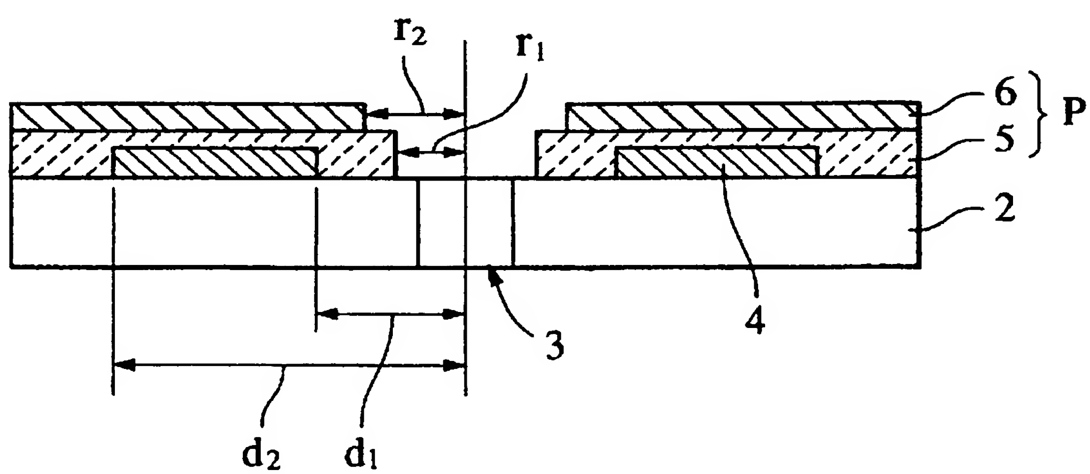


FIG. 1

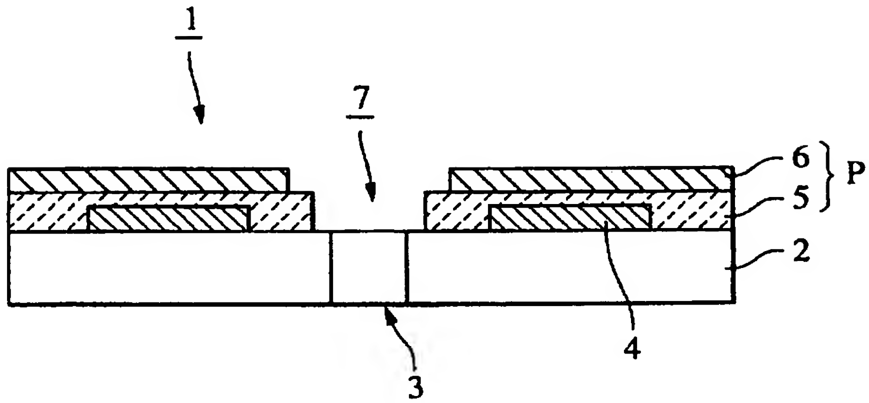


FIG. 2

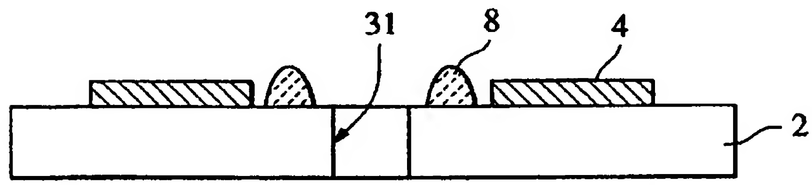


FIG. 3

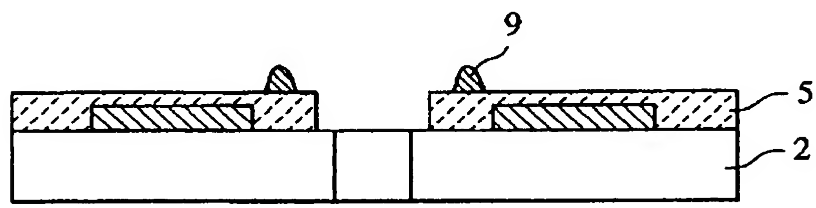
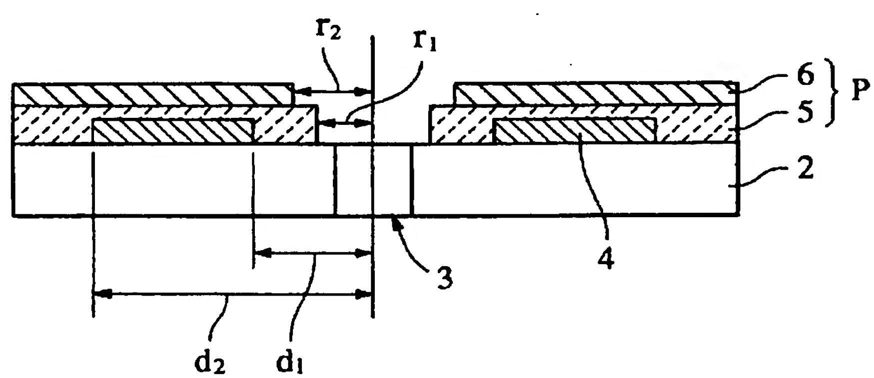


FIG. 4



OPTICAL RECORDING MEDIUM AND PROCESS FOR PRODUCING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an optical recording medium, and a process for producing such a medium, upon which at least one of recording, reproducing and erasing of information is optically performed.

2. Related Background Art

Recently, rewritable optical disks have been marketed and increasingly have been used as files for code data and images in computers. However, in such disks, recording, reproducing or erasing is conducted by using a laser beam. Thus, errors sometimes occur in reading or recording data if dust particles or flaws are present on a laser beam incident surface of a substrate of the disk. For example, in a magnetooptical disk, and particularly in a magnetooptical disk in a magnetic field modulation recording system which employs a magnetic head, either the recording medium or the device may be broken due to electrostatic contact between the magnetic disk and a protective layer, which may be caused by dust particles on the protective layer or by operation in an atmosphere at low humidity. Therefore, investigation has been made as to the possibility of providing a protective layer containing an antistatic agent and a lubricant on each of the laser beam incident surface and the recording layer of a substrate, for preventing adhesion of dust particles and flaws. On the other hand, it has been known that the addition of an antistatic agent and a lubricant to the protective layer causes corrosion and blister formation in the recording layer. Thus, investigation has also been made as to the possibility of providing a two-layer structure comprising a first protective layer containing no additive and a second protective layer containing an antistatic agent, etc., and a multi-layer protective layer comprising a first protective layer, a second protective layer and an intermediate protective layer for improving adhesion between the first and second protective layers, and correcting warping of a substrate (Japanese Patent Application No. 4-125873).

Examples of known methods of producing an optical recording medium comprising such a multi-layer protective layer include a method of successively laminating photo-curable resin layers and a method of successively laminating resin sheets.

A possible method of forming, with good productivity, a multi-layer protective layer comprising laminated photo-cured resin layers on a disk substrate is a method comprising coating a photo-curable resin composition for forming a first protective layer by a spin coating method, curing the resin composition to form the first protective layer, coating a photo-curable resin composition for forming a second protective layer by the spin coating method and then curing the resin composition to form the second protective layer.

However, stripe marks caused by a flow of an uncured photo-curable resin composition are sometimes observed on the surface of the multi-layer protective layer formed by this method. This causes the formation of a disk comprising a protective layer having a nonuniform thickness. Such a disk comprising a protective layer having a nonuniform thickness becomes an inferior product because of its poor appearance, and consequently decreases productivity.

When a magnetooptical recording medium, and particularly a magnetooptical recording medium for recording data thereon in a magnetic field modulation system, is produced

by the above-described process, the magnetic head may be broken due to collision between the magnetic head and the protective layer having a nonuniform thickness, or recorded data is lost due to breakage of the magnetooptical recording medium.

SUMMARY OF THE INVENTION

The present invention has been achieved in consideration of the above problems, and an object of the present invention is to provide an optical recording medium having an excellent appearance even when a multi-layer protective layer is formed by a spin coating method.

Another object of the present invention is to provide an optical recording medium which minimizes or eliminates produces recording errors.

Another object of the present invention is to provide a process for producing, with good productivity, an optical recording medium comprising a multi-layer protective layer, which minimizes or eliminates inferior products.

According to an aspect of the present invention, there is provided an optical recording medium comprising an optically transparent substrate having an opening, a recording layer and a protective layer, both of which are formed on the substrate, wherein the protective layer has an opening whose center coincides with the opening of the substrate and which is larger than the opening of the substrate.

According to another aspect of the present invention, there is provided a process for producing an optical recording medium comprising an optically transparent substrate having an opening, a recording layer and a protective layer, both of which are formed on the substrate comprising forming the protective layer on the substrate so as to coat the recording layer, and providing an opening in the protective layers whose center coincides with the opening of the substrate and which is larger than the opening of the substrate.

According to another aspect, the present invention relates to a method for manufacturing an optical recording medium comprising the steps of providing an optically transparent disk-shaped substrate having an opening defined by an opening periphery located at a central portion thereof, forming a recording layer on the substrate, and forming a protective layer on at least a portion of the substrate and the recording layer by depositing an annular ring of photocurable resin material on the substrate, around the opening periphery of the opening in the substrate, spin-coating the annular ring of photocurable resin material over at least a portion of the substrate and the recording layer, and photo-curing the photocurable resin material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic sectional view of an optical disk in accordance with an embodiment of the present invention;

FIG. 2 is a schematic drawing illustrating a process for producing the optical disk shown in FIG. 1 in accordance with another embodiment of the present invention;

FIG. 3 is a schematic drawing illustrating a process for producing the optical disk shown in FIG. 1 in accordance with a further embodiment of the present invention; and

FIG. 4 is a schematic drawing illustrating a first embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

Embodiments of the present invention are described below with reference to the drawings.

In FIG. 1, reference numeral 1 denotes a magnetooptical disk; reference numeral 2 denotes a substrate having a center hole 3; reference numeral 4 denotes a magnetooptical recording layer; and reference numeral 5 denotes a multi-layer protective layer P comprising a first protective layer 5 and a second protective layer 6.

The first and second protective layers are formed in an annular form on the substrate 2 so that the diameter of an opening of the second protective layer 6 is greater than the diameter of an opening of the first protective layer 5.

On the magnetooptical disk, as shown in FIG. 2, a photo-curable resin composition 8 is provided in an annular form on the substrate 2 having the recording layer 4 formed thereon, in the vicinity of the center hole 3, and the photo-curable resin composition 8 is then spread by rotating the substrate 2 to coat the recording layer 4 with the resin composition 8. Thereafter, the photo-curable resin composition is cured by irradiation with light to form the first protective layer 5. It is preferable that the diameter of an opening 7 of the first protective layer 5 is larger than the diameter of the center hole 3 of the substrate 2.

Specifically, to obtain an optical recording medium having an excellent appearance and causing minimum or no recording errors, it is preferable that the photo-curable resin composition for forming the first protective layer 5 is applied or deposited as an annular ring in the vicinity of the center hole 3 of the substrate 2, and then spin-coated so as not to drop into the center hole 3 of the substrate 2 on side wall 31.

Namely, in a spin coating technique, the rotational speed is generally increased during the final stage of the coating step, before the coating step is completed.

For example, even if the resin material drops into the center hole 3 on the side wall 31, as described above, then resin material located on the side wall 31 of the center hole 3 may be returned to the surface of the first protective layer and radially spread out on the surface thereof by centrifugal force, when the rotational speed is increased at the end of the spin-coating process to make the surface of the resin composition for first protective layer flat and smooth. As a result, resin marks may remain on the surface of the first protective layer 5 and thus deteriorate not only the appearance of the surface of the first protective layer 5 but also the smoothness of the first protective layer 5, thereby causing head crash.

In order to prevent the photo-curable resin composition for forming the first protective layer 5 from dropping into the center hole 3 on the side wall 31 of the substrate 2 during the step of applying the resin composition in the vicinity of the center hole 3 of the substrate 2 and the subsequent spin coating step, it is effective to control the angle of contact between the resin composition and the substrate, the position of deposition of the resin composition, etc. For example, it is preferable to appropriately set the above coating conditions so as to prevent the resin composition from sufficiently spreading during the time the resin composition is supplied to a portion in the vicinity of the center hole of the substrate.

Referring now to FIG. 3, like the first protective layer 6, the second protective layer on the first protective layer 5 is formed by depositing an annular ring of a photo-curable resin composition 9 for forming the second protective layer 6, spreading the resin composition 9 by rotating the substrate 2 and then curing the resin composition by irradiation with light.

The diameter of an opening of the second protective layer 6 is preferably greater than that of the opening of the first protective layer 5. Namely, in order to prevent the photo-curable resin composition for forming the second protective layer from dropping into the opening on side wall 31 of the center hole 3 of the substrate 2 during the step of depositing the resin composition in the vicinity of the center hole 3 of the substrate 2 and the subsequent spin coating step, it is effective to control the angle of contact between the resin composition for forming the second protective layer and the substrate, the position of deposition of the resin composition, etc. For example, it is preferable to appropriately set the above coating conditions so as to prevent the resin composition from sufficiently spreading during the time the resin composition is supplied to a portion in the vicinity of the center hole of the substrate.

Although this embodiment relates to an optical recording medium having a multi-layer protective layer comprising two protective layers, the technology of the present invention is also useful for an optical recording medium having a multi-layer protective layer comprising three or more protective layers. Specifically, an optical recording medium having a multi-layer protective layer can be produced by using the spin coating method in which the diameter of an opening of a (n+1)th protective layer (n is an integer of 1 or more) in the multi-layer protective layer from the side of the recording layer is greater than the diameter of an opening of a (n)th protective layer.

In the embodiment of the present invention, the photo-curable resin compositions for the multi-layer protective layer are not limited as long as they have no adverse effect on the recording layer and satisfy the above-described characteristics. For example, acrylic ultraviolet curing resins and the like can be used. An example of such resins is a composition comprising prepolymer component (A), monomer component (B) serving as a reactive diluent, and photopolymerization initiator component (C) at a ratio of components (A), (B) and (C) in which the ratio of component (A) : component (B)=5 to 95: 95 to 5 (ratio by weight), and the concentration of component (C) is 0.1 to 10% by weight of the total amount.

Examples of component (A) include polyol polyacrylates (polyhydric alcohol or polyether polyacrylates), particularly, at least trifunctional polyol polyacrylates, such as pentaerythritol triacrylate, dipentaerythritol hexaacrylate, and the like; modified polyol polyacrylates (polyacrylates of polyols modified by epoxide or lactone or diacrylates of modified diols obtained by adding epoxide to polyhydroxy phenols such as bisphenol A or bisphenol S); polyester acrylates (produced by condensation telomerization of polyhydroxy alcohols, polybasic acids or anhydrides thereof and acrylic acid); urethane acrylates (produced by reaction of polyols such as polyether polyols or polyester polyols, polyisocyanate and acrylates having a hydroxyl group); epoxy acrylates (oligomers obtained by adding acrylic acid or acrylates having a terminal carboxyl group to epoxy compounds); bisphenol A diglycidyl ethers; novolak polyglycidyl ethers and the like. Particularly, at least trifunctional polyol polyacrylates having excellent curing properties and high surface hardness are preferable.

Examples of component (B) include acrylates of polyhydroxy alcohols, particularly, polyfunctional acrylic monomers, for example acrylates such as ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol diacrylate, butylene glycol diacrylate, neopentyl glycol diacrylate, 1,4-butanediol diacrylate, 1,4-hexanediol diacrylate, pentaerythritol diacrylate and the like; triacrylates such as pentaerythritol triacrylate, trimethylolpropane triacrylate and the like. Any one of these compounds or a mixture comprising at least two of these compounds can be used as component (B).

Although any known photopolymerization initiators can be used as component (C), initiators exhibiting good storage stability after mixing are preferable. Examples of such initiators include benzoin alkyl ether types such as benzoin ethyl ether, benzoin isobutyl ether and the like; acetophenone types such as 2,2'-diethoxyacetophenone, 4'-phenoxy-2,2-dichloroacetophenone, and the like; propiophenone types such as 2-hydroxy-2-methylpropiophenone, 4'-isopropyl-2-hydroxy-2-methylpropionphenone and the like; anthraquinone types such as benzyl methyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2-ethyl anthraquinone and 2-chloroanthraquinone and the like; thioxanthone types such as 2,4-dimethyl thioxanthone, Michler's ketone and the like. Any one of these compounds or a mixture of at least two compounds at any desired ratio can be used.

A recording layer which is generally used for optical recording, such as a recording layer containing an organic dye, e.g., a polymethine dye or cyanine dye, a magnetooptical recording layer containing a rare earth metal or transition metal, can be used as the recording layer.

When a light beam for at least one of recording, reproduction and erasing information is applied to the optical recording medium through the substrate, the substrate is preferably transparent to the light beam. Preferable examples of such substrates include substrates comprising bisphenol A type polycarbonate, acrylic resin, methacrylic resin, polystyrene resin, polyolefin resin and the like.

As described above, when the multi-layer protective layer is formed, the (n+1)th protective layer is formed so as to have an opening larger than the opening of the (n)th protective layer, thereby preventing the occurrence of nonuniformity of the thickness due to stripe marks.

In addition, the angle of contact between the curable resin for the second protective layer and the first protective layer is larger than the angle of contact between the curable resin for the first protective layer and the substrate, thereby facilitating control of the coating positions of the curable resins and the thicknesses of the layers, and thus improving productivity.

Further, the angle of contact between the curable resin for the (n+2)th protective layer and the (n+1)th protective layer (n is an integer of 1 or more) is larger than the angle of contact between the curable resin for the (n+1)th protective layer and the (n)th protective layer, thereby facilitating control of the resin coating positions and the thicknesses of the layers, and thus improving productivity.

A number of embodiments of the present invention will now be explained in more detail with reference to the following examples.

EXAMPLE 1

As shown in FIG. 4, on a polycarbonate disk substrate 2 having a diameter of 86 mm (with an opening 3 having a diameter of 15 mm) an annular magnetooptical recording layer 4 was formed, by a sputtering method, so as to be concentric with the disk substrate 2. The recording layer 4 comprised an inorganic protective layer, a magnetic layer, an inorganic protective layer and a reflecting layer, the radii (d1) and (d2) of small and large circles of the annular recording layer 4 being 20 mm and 42.5 mm, respectively.

An epoxyacrylate ultraviolet curable resin (Trade Name: MH-7210; produced by Mitsubishi Rayon Co., Ltd.) having a surface tension of about 29 mN/m at 23° C. was circumferentially supplied in an annular form whose center coincided with the center hole 3 of the substrate 2 and which had a radius of 16.5 mm, as shown in FIG. 2. The curing resin

was then coated in a thickness of about 6 μm by a spin coating method on a doughnut-like annular region concentric with the center hole 3 and surrounded by circles having a radii of 16 mm and 43 mm to cover the recording layer 4. The curing resin was then irradiated with ultraviolet light to form a first protective layer 5. An ultraviolet curing epoxy-acrylate resin (Trade Name: EX-841; produced by Dainippon Ink Co., Ltd.) having a surface tension of about 37 mN/m at 23° C. was supplied in an annular form whose center coincided with the center hole 3 of the substrate 2 and which had a radius of 16.5 mm, on the first protective layer, and was then spin-coated to form a second protective layer 4 of about 4 μm thickness In this way, a magnetooptical disk with a multi-layer protective layer P was formed.

As a result, the radius r_1 of the opening of the first protective layer 5 formed by curing was about 16 mm, and the radius r_2 of the opening of the second protective layer 6 was 16.2 mm. The angle of contact between the material for the first protective layer 5 and the substrate 2 was about 30°, and the angle of contact between the material for the second protective layer 6 and the first protective layer 5 was about 60°. In this example, materials having different surface tensions were used in order to cause the different contact angles. Namely, a material having a surface tension lower than that of the material for the second protective layer 6 was used for the first protective layer 5 so that the angle of contact between the material for the first protective layer 5 and the substrate 2 was smaller than the angle of contact between the material for the second protective layer 6 and the first protective layer 5. This increased the contact angle of the material for the upper second protective layer 6 and thus facilitated control of the coating positions and of the thicknesses of the layers, thereby improving productivity.

EXAMPLE 2

A magnetooptical disk was produced in the same manner as in Example 1 except that an ultraviolet curable epoxy-acrylate resin (Trade Name: EX-841; produced by Dainippon Ink Co., Ltd.) having a surface tension of about 37 mN/m was used as a material for the first protective layer 5 under heating at about 40° C., and the same ultraviolet curable epoxyacrylate resin as the resin used for the first protective layer 5 was used as the material for the second protective layer 6 under cooling at about 15° C.

As a result, the radius r_1 of the opening of the first protective layer 5 formed by curing was about 16 mm, and the radius r_2 of the opening of the second protective layer 6 was 16.3 mm. The angle of contact between the material for the first protective layer 5 and the substrate 2 was about 30°, and the angle of contact between the material for the second protective layer 6 and the first protective layer 5 was about 63°. In this example, the respective resin materials were coated at different temperatures in order to cause different contact angles. Namely, the coating temperature of the material for the first protective layer 5 was relatively high, and the coating temperature of the material for the second protective layer 6 was relatively low so that the angle of contact between the material for the first protective layer 5 and the substrate 2 was smaller than the angle of contact between the material for the second protective layer 6 and the first protective layer 5. In this way, since the contact angle of the material used can be changed by temperature control, various materials can be used without being restricted by surface tension and viscosity.

EXAMPLE 3

A magnetooptical disk was produced in the same manner as that in Example 1, except that the material for the second

protective layer 6 was circumferentially supplied in an annular form which was concentric with the center hole 3 of the substrate 2 and which had a radius of 17.5 mm. As a result, the radius (r_2) of the opening of the second protective layer 6 was 17.2 mm.

EXAMPLE 4

A magnetooptical disk was produced in the same manner as that in Example 2, except that the material for the second protective layer 6 was circumferentially supplied in an annular form which was concentric with the center hole 3 of the substrate 2 and which had a radius of 17.5 mm. As a result, the radius (r_2) of the opening of the second protective layer 6 was 17.3 mm.

EXAMPLE 5

A recording layer 4 was formed on a polycarbonate substrate 2 in the same manner as that in Example 1. An ultraviolet curable urethane acrylate resin (Trade Name:SD-301; produced by Dainippon Ink Co., Ltd.) having a surface tension of about 40 mN/m at 23° C. was circumferentially supplied in an annular form which was concentric with the center hole 3 of the substrate 2 and which had a radius of 16.5 mm. The curing resin was then coated, by a spin coating method, on a doughnut-like annular region surrounded by a circle which was concentric with the center hole 3 and which had a radius of 43 mm and a circle which was concentric with the center hole 3 and which had a radius of 16 mm, to form a resin layer having a thickness of 6 μm for coating the recording layer 4. The resin layer was then cured by irradiation with ultraviolet light to form the first protective layer 5.

An ultraviolet curable epoxyacrylate resin (Trade Name: MH-7210; produced by Mitsubishi Rayon Co., Ltd.) having a surface tension of about 26 mN/m at 23° C. and containing an antistatic agent was circumferentially supplied in an annular form which was concentric with the center hole 3 and which had a radius of 19.5 mm, on the first protective layer 5. The resin was coated to a thickness of about 4 μm on the first protective layer 5 by a spin coating method, and then irradiated with ultraviolet light to form the second protective layer 6. In this way, a magnetooptical disk was obtained.

As a result, the radius r_1 of the opening of the first protective layer 5 was about 16 mm, and the radius r_2 of the opening of the second protective layer 6 was about 17.5 mm. The angle of contact between the material for the first protective layer 5 and the substrate 2 was about 60°, and the angle of contact between the material for the second protective layer 6 and the first protective layer 5 was about 30°. However, since the radii of the small circles of the annular forms were different in coating the respective resins, the magnetooptical disk obtained in this example caused no streak having a nonuniform thickness or visually recognizable on the surface of the second protective layer 6, thereby increasing the yield of the magnetooptical disk.

COMPARATIVE EXAMPLE 1

A magnetooptical disk was produced in the same manner as that in Example 5, except that the photo-curable resin composition for the second protective layer 6 was circumferentially supplied in an annular form which was concentric with the center hole 3 and which had a radius of 16.5 mm, on the first protective layer 5.

As a result, stripes radially extending from the opening of the second protective layer 6 were observable with the eye on the second protective layer 6, and the thickness of a portion of the second protective layer 6 where the stripes were observed was greater than a predetermined thickness of 4 μm. The magnetooptical disk of this example was thus unsuitable as a magnetooptical disk, particularly as a magnetooptical disk in a magnetic field modulation recording system.

EXAMPLE 6

100 magnetooptical disks were produced in the same manner as in EXAMPLE 1, and the percentage of magnetooptical disks free from a conspicuous streak on the second protective layer 6 was measured.

The results are shown in Table 1.

EXAMPLE 7

100 magnetooptical disks were produced in the same manner as in EXAMPLE 2.

EXAMPLE 8

100 magnetooptical disks were produced in the same manner as in EXAMPLE 3.

EXAMPLE 9

100 magnetooptical disks were produced in the same manner as in EXAMPLE 4.

EXAMPLE 10

100 magnetooptical disks were produced in the same manner as in EXAMPLE 5.

COMPARATIVE EXAMPLE 2

100 magnetooptical disks were produced in the same manner as in COMPARATIVE EXAMPLE 1.

The magnetooptical disks produced in each of EXAMPLEs 7, 8, 9 and 10 and COMPARATIVE EXAMPLE 2 were evaluated in the same manner as in EXAMPLE 6.

The results are shown in Table 1.

TABLE 1

	Number of disks with streak defect	Number of good disks	Yield
EXAMPLE 6	3	97	97%
EXAMPLE 7	3	97	97%
EXAMPLE 8	0	100	100%
EXAMPLE 10	4	96	96%
COMPARATIVE EXAMPLE 2	40	60	60%

Thus, those skilled in the art readily will appreciate that the preferred embodiments achieve each of the above-listed objects of the inventions.

While the present invention has been described with respect to what is presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, the present invention includes various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

What is claimed is:

1. An optical recording medium comprising:

an optically transparent substrate having an opening defined by an opening perimeter;

a recording layer formed on the substrate; and

a multilayer protective layer comprised of a plurality of protective layers successively formed on at least a portion of said substrate and said recording layer, wherein each of said plurality of protective layers has an opening defined by a respective opening perimeter, each of said openings of said plurality of protective layers being larger than the opening of the substrate, such that the opening perimeter of the opening in said substrate is located within the opening perimeter the opening in each of said plurality of protective layers, and wherein a diameter of an opening of an (n+1)th protective layer in the multilayer protection layer is larger than a diameter of an opening of an (n)th protective layer, wherein "n" is an integer not less than 1.

2. An optical recording medium according to claim 1, wherein said substrate is disk-shaped.

3. An optical recording medium according to claim 2, wherein a center of the opening of said protective layer coincides with a center of the opening of said substrate.

4. An optical recording medium according to claim 3, wherein each of the opening of said substrate and the opening of said protective layer has a round shape.

5. An optical recording medium according to claim 2, wherein each of the opening of said substrate and the opening of said protective layer has a found shape.

6. An optical recording medium according to claim 1, wherein a center of the opening of said protective layer coincides with a center of the opening of said substrate.

7. An optical recording medium according to claim 6, wherein each of the opening of said substrate and the opening of said protective layer has a round shape.

8. An optical recording medium according to claim 1, wherein each of the opening of said substrate and the opening of said protective layer has a round shape.

9. An optical recording medium according to claim 1, wherein the protective layer comprises a photo-cured resin composition.

10. An optical recording medium according to claim 1, wherein each of the plurality of protective layers in the multilayer protective layer comprises a photo-cured resin.

11. An optical recording medium according to claim 1, wherein said multilayer protective layer comprises a first protective layer formed on at least a portion of said substrate, and a second protective layer formed on said first protective layer, said first protective layer comprising a photo-cured resin composition, the resin composition before being cured having a first contact angle with said substrate when disposed on said substrate, and said second protective layer comprising a photo-cured resin composition, the resin composition before being cured having a second contact angle with said first protective layer when disposed on said first protective layer, said first contact angle being smaller than said second contact angle.

12. An optical recording medium according to claim 1, wherein the (n+1)th layer in the multilayer protective layer comprises a photo-cured resin composition, the resin composition before being cured having a first contact angle with the (n) th layer when disposed on the (n) th layer, and wherein an (n+2)th protective layer comprises a photo-cured resin composition, said resin composition before being cured having a second contact angle with the (n+1)th protective layer, said first contact angle being smaller than said second contact angle.

13. An optical recording medium according to claim 1, wherein the multilayer protective layer comprises a first protective layer provided on the recording layer and a second protective layer provided on the first protective layer, the first protective layer containing no additives, and the second protective layer containing an antistatic agent or lubricant.

14. A process for producing an optical recording medium comprising the steps of:

providing an optically transparent substrate having an opening;

forming a recording layer on the substrate; and

forming a multilayer protective layer comprising a plurality of successively formed protective layers on at least a portion of the substrate and the recording layer, each of said plurality of protective layers having a respective opening having a center that coincides with a center of the opening of the substrate, each of said respective openings being larger than the opening of the substrate, and wherein an opening of an (n+1)th protective layer in the multilayer protective layers is larger than a diameter of an opening of an (n)th protective layer, where "n" is an integer not less than 1.

15. A process for producing an optical recording medium according to claim 14, wherein each of the opening of the substrate and the opening of the protective layer has a round shape.

16. A process for producing an optical recording medium according to claim 14, wherein each of the successively formed protective layers of said multilayer protective layer comprises a photo-cured resin.

17. A process for producing an optical recording medium according to claim 14, wherein the step of forming a plurality of successively formed protective layers includes;

forming a first protective layer comprising a photo-cured resin composition, the resin composition before being cured having a first contact angle with the substrate when disposed on the substrate, and

forming a second protective layer comprising a photo-cured resin composition, the resin composition before being cured having a second contact angle with the first protective layer when disposed on the first protective layer, the first contact angle being smaller than the second contact angle.

18. A process producing an optical recording medium according to claim 14, wherein the step of forming a plurality of successively formed protective layers includes;

forming an (n+1)th protective layer comprising a photo-cured resin composition, the resin composition before being cured having a first contact angle with an (n)th protective layer when disposed on the (n) th protective layer, and

forming an (n+2)th protective layer comprising a photo-cured resin composition, the resin composition before being cured having a second contact angle with the (n+1)th protective layer when disposed on the (n+1)th protective layer, the first contact angle being smaller than the second contact angle.

19. A process for manufacturing an optical recording medium according to claim 18, wherein the step of forming a plurality of successively formed protective layers includes:

forming a first protective layer comprising a photo-cured resin composition on the substrate directly, the resin composition before being cured having a third contact

angle with the substrate when disposed on the substrate, and

forming a second protective layer comprising a photocured resin composition, the resin composition before being cured having a forth contact angle with the first protective layer when disposed on the first protective layer, the third contact angle being smaller than the forth contact angle.

20. A method for manufacturing an optical recording medium comprising the steps of:

providing an optically transparent disk-shaped substrate having an opening defined by an opening periphery located at a central portion thereof;

forming a recording layer on the substrate;

successively forming a plurality of protective layers on at least a portion of the substrate and the recording layer, wherein each of the plurality of protective layers is formed by

depositing an annular ring of photocurable resin material on the substrate, around the opening periphery of the opening in the substrate, or on a preceding protective layer around an opening periphery of a respective openings in the preceding protective layer;

spin-coating the annular ring of photocurable resin material over at least a portion of the substrate and the recording layer, and

photo-curing the photocurable resin material; and

wherein positions where respective annular rings of photocurable resin material are disposed and selected such that each of the openings of the protective layer is larger than the opening of the substrate and the opening of the respective preceding protective layer.

21. A method for manufacturing an optical recording medium according to claim 20, wherein said forming step includes controlling a coating temperature of the respective photocurable resin materials.

22. A method for manufacturing an optical recording medium according to claim 20, wherein said forming step includes controlling a surface tension or viscosity of the respective photocurable resin materials.

* * * * *

Appendix B

US005674649A

United States Patent [19]

Yoshioka et al.

[11] **Patent Number: 5,674,649**

[45] **Date of Patent: Oct. 7, 1997**

[54] **METHOD OF RECORDING INFORMATION**

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[73] Assignee: **Matsushita Electric Industrial Co., Ltd.**, Kadoma, Japan

[21] Appl. No.: **636,494**

[22] Filed: **Apr. 23, 1996**

Related U.S. Application Data

[62] Division of Ser. No. 452,497, May 30, 1995.

[30] **Foreign Application Priority Data**

Jun. 13, 1994 [JP] Japan 6-155186

[51] **Int. Cl.**^{6} **G11B 7/00**

[52] **U.S. Cl.** **430/19**; 430/270.13; 430/945; 369/284

[58] **Field of Search** 430/269, 945, 430/270.13, 19; 369/121, 124, 284

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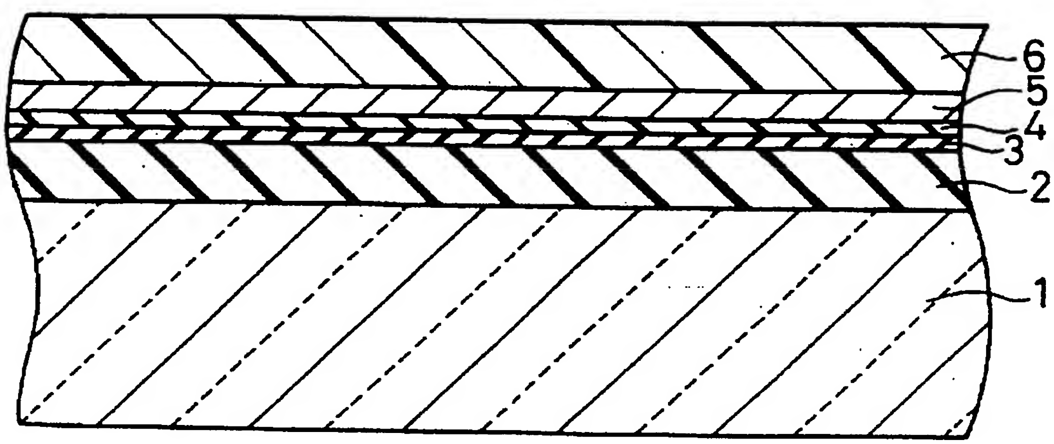
Primary Examiner—John A. McPherson
Attorney, Agent, or Firm—Morrison & Foerster LLP

[57] **ABSTRACT**

On one surface of a disk substrate, a first dielectric layer, a thin recording layer, a second dielectric layer and a reflecting layer are cumulatively formed. The second dielectric layer is thinner than the first dielectric layer and is 35–70 nm thick. The reflecting layer is 70–120 nm thick. The total thickness of the four layers is 250–430 nm. The compressive stress of the layers is offset by tensile stress generated by an overcoat resin protective layer, formed on the reflecting layer. A method of using the optical recording medium applies the MCAV (Modified Constant Angular Velocity) recording method which records information by changing recording frequencies in accordance with linear velocity. The linear velocity is 5–12 m/s. A ratio of an inner circumference recording pulse width to an outer circumference recording pulse width is 1.2 or more.

12 Claims, 4 Drawing Sheets



F I G. 1

FIG. 2A

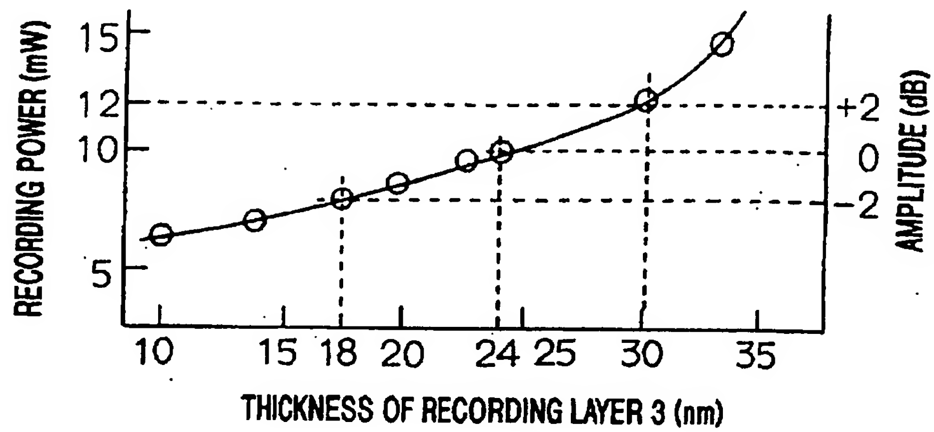


FIG. 2B

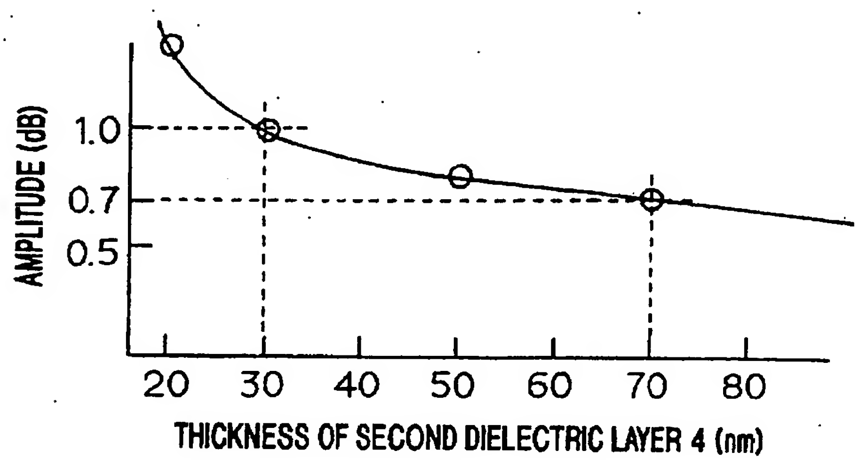
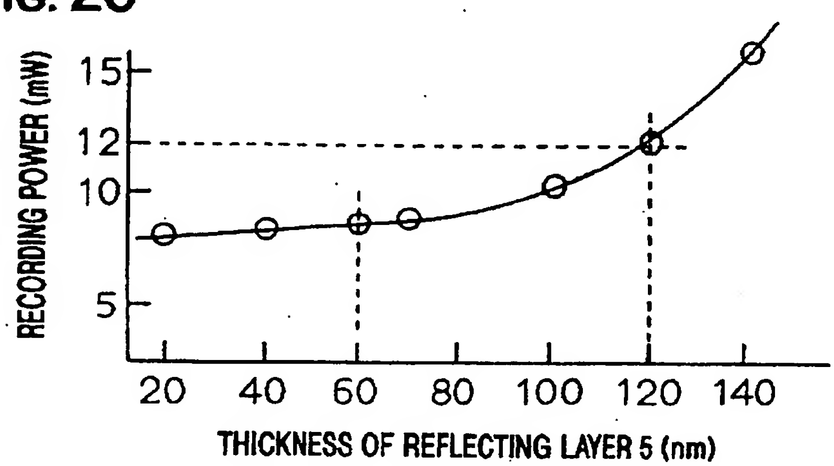


FIG. 2C



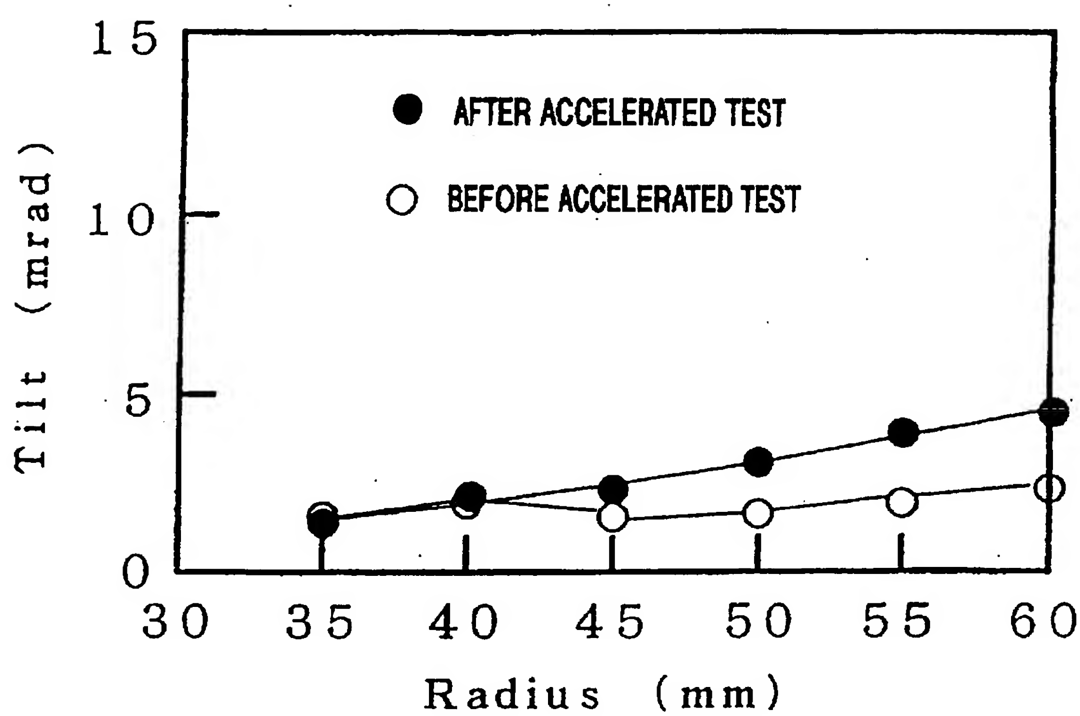

15
10
5
0
Tilt (mrad)
AFTER ACCELERATED TEST
BEFORE ACCELERATED TEST
30
35
40
45
50
55
60
Radius (mm)

FIG. 3

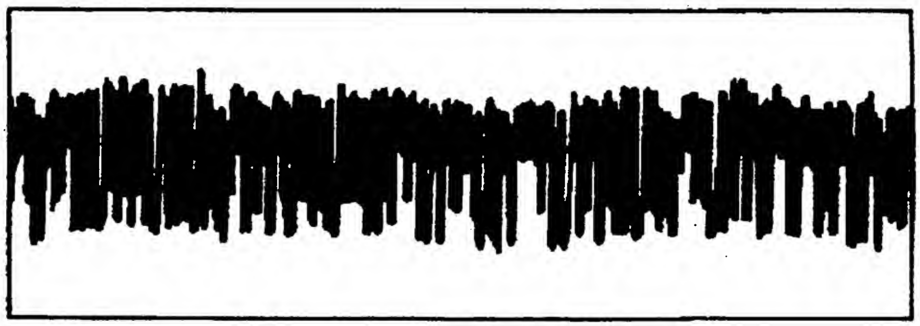


FIG. 4

METHOD OF RECORDING INFORMATION

This application is a division of U.S. application Ser. No. 08/452,497 filed May 30, 1995 now allowed.

FIELD OF THE INVENTION

The invention relates to an optical recording medium (indicated as a disk hereinafter) which can record, reproduce and delete information at high density and capacity by a laser beam or the like, and further relates to a method of using the optical recording medium.

BACKGROUND OF THE INVENTION

Reloadable disks are conventionally used for many purposes. A disk typically includes a disk-type transparent substrate, and a thin recording layer on one surface of the substrate. Data is repeatedly recorded and deleted by reversibly changing the optical density of the thin recording layer. The thin recording layer of the disk is crystallized in advance, and is then heated, melted and quenched by irradiating the thin recording layer with about a 1 μm laser beam and changing the intensity of the beam. As a result, the layer becomes amorphous and records information. In addition, the amorphous recording thin layer is crystallized by raising the temperature of the layer in a range between the crystallization temperature and the melting point and then annealing the layer, thus deleting information.

When a resin substrate, for example, is used for the disk-thin recording layer is formed directly on the substrate, the substrate is heated to a high temperature in a minute section of about 1 μm by recording and deleting and is thus deformed. Therefore, in general, a dielectric layer is formed as a heat insulating layer between the substrate and the thin recording layer and between the thin recording layer and a layer protecting the thin recording layer (protective layer), thus preventing thermal deformation of the substrate. Since the temperature rise, quenching and annealing properties of the thin recording layer vary due to the heat conduction properties of the protective layer, recording and deleting characteristics of the disk are improved by selecting preferable materials and layer composition. Furthermore, the recording and deleting characteristics of the disk are improved by forming a reflecting layer on the surface of the dielectric layer facing the protective layer and utilizing the multiple interference of a laser beam. This four-layer disk structure is generally well known.

A rapid cooling disk structure is proposed for the four-layer reloadable disk. In the rapid cooling disk structure, the dielectric layer between the thin recording layer and the reflecting layer (identified as a second dielectric layer hereinafter) is thinned so that heat generated in the thin recording layer during recording and deleting is quickly released to the reflecting layer. The rapid cooling disk structure has an advantage in that the outer limits of the erase rate and power improve since the temperature of the dielectric layers on both sides of the thin recording layer rises by widely dispersing the heat from the thin recording layer. It is also advantageous in making the thin recording layer amorphous since the layer is cooled quickly in this structure. Japanese Patent Application No. Sho 63-207040 (Published Unexamined (Laid-open) Japanese Patent Application No. Hei 02-056746) discloses a rapid cooling disk structure. In this application, the second dielectric layer is thinner than the dielectric layer between the disk substrate and the thin recording layer (identified as a first dielectric layer hereinafter) and is 30 nm thick or less.

However, when the thickness of the second dielectric layer is 30 nm or less, the recording and deleting sensitivities of the disk decline, so that an expensive high power semiconductor laser has to be used. In addition, the first and the second dielectric layers are under thermal stress, expanding and shrinking due to rapid heating at 400° C. or higher and cooling for repeated recording and deleting. Although the second dielectric layer has a smaller heat load than the first dielectric layer, the layer repeatedly receives thermal stress. The layer should thus have a proper thickness. The thickness of the second dielectric layer has to be selected in consideration not only of the heat conduction but also of optical properties.

SUMMARY OF THE INVENTION

It is an object of this invention to solve the above-mentioned problem by providing an optical recording medium, which has high recording sensitivity and is excellent in recording and deleting repeatedly, and a method of using the optical recording medium.

In order to accomplish these and other objects and advantages, the optical recording medium includes a transparent substrate, a first dielectric layer formed on one surface of the transparent substrate, a thin recording layer which is formed on the first dielectric layer, a second dielectric film formed on the thin recording layer, and a reflecting layer formed on the second dielectric layer. The thin recording layer has properties of becoming amorphous after its temperature is increased, then melting and quenching by absorbing energy from the irradiation of a laser beam, and of crystallizing its amorphous state by temperature rise. The second dielectric layer is thinner than the first dielectric layer and is 35–70 nm thick, and the thickness of the reflecting layer is 70–120 nm.

It is preferable that the thin recording layer is 18–30 nm thick. The first dielectric layer preferably is 140–210 nm thick. The first and the second dielectric layers preferably contain ZnS at 60–95 mol % and SiO_2 at 5–40 mol %.

The reflecting layer preferably contains Al as a main material and at least one metal selected from the group comprising Ti, Ni, Cr, Cu, Ag, Au, Pt, Mg, Si and Mo.

The thin recording layer preferably contains Te, Ge and Sb, and preferably also contains nitrogen. The thin recording layer preferably contains GeTe, Sb_2Te_3, Sb and nitrogen.

The thin recording layer is preferably composed so that $0.2 \leqq b \leqq 0.5$ where b is the mol ratio of Sb/Sb_2Te_3.

The optical recording medium preferably further includes a 3–15 μm thick overcoat protective layer on the reflecting layer, and that the protective layer, which preferably generates tensile stress.

It is preferable that the overcoat resin is annealed for stress relaxation.

The first dielectric layer, the thin recording layer, the second dielectric layer and the reflecting layer are preferably 250–430 nm thick altogether, and preferably have 0.5×10^9 dyn/cm² or less compressive stress.

The optical recording medium preferably is recorded with information on one surface, and an angle where a tangent of the surface and the horizontal reference plane of the medium intersect each other is preferably 1–2 mrad so as to protrude the surface.

The transparent substrate preferably has a convex surface. An angle where a tangent of the convex surface and the horizontal reference plane of the substrate intersect each other is preferably 1–2 mrad, and the first dielectric layer, the

thin recording layer, the second dielectric layer and the reflecting layer are preferably cumulatively formed on the convex surface.

The method of using an optical recording medium of the invention applies the MCAV (Modified Constant Angular Velocity) recording method which records by varying recording frequencies in accordance with linear velocity. The linear velocity is 5–12 m/s. The recording pulse width of the inner circumference is larger than that of the outer circumference, and the ratio of the inner circumference recording pulse width to the outer circumference recording pulse width is 1.2 or above. The optical recording medium includes a transparent substrate, a first dielectric layer formed on one surface of the transparent substrate, a thin recording layer formed on the first dielectric layer, a second dielectric film formed on the thin recording layer, and a reflecting layer formed on the second dielectric layer. The thin recording layer has properties of becoming amorphous after its temperature is increased, then melting and quenching by absorbing energy from the irradiation of a laser beam, and of crystallizing its amorphous state by temperature rise. The second dielectric layer is thinner than the first dielectric layer and is 35–70 nm thick, and the thickness of the reflecting layer is 70–120 nm.

The recording pulse width preferably is 40–60 ns at 5 m/s linear velocity and is 30–40 ns at 12 m/s.

The MCAV recording method preferably is applied so as to record information by varying a record starting point at the maximum of 7.75 μm in 5–12 m/s linear velocity.

The optical recording medium comprises the transparent substrate, the first dielectric layer, the thin recording layer, the second dielectric film, and the reflecting layer. The thin recording layer has the above-mentioned properties. The second dielectric layer is thinner than the first dielectric layer and is 35–70 nm thick, and the thickness of the reflecting layer is 70–120 nm. Thus, the optical recording medium has high recording sensitivity and excellent repeated recording and deleting properties.

A mixed material of ZnS and SiO_2 having excellent heat resisting properties and relatively small heat conduction is used for the first and the second dielectric layers. The second dielectric layer is 35–70 nm thick, and has not only excellent optical properties but also mechanical strength. The second dielectric layer widens the distance between the thin recording layer and the reflecting layer, and slows down the cooling speed of the thin recording layer. As a result, the recording sensitivity of the optical recording medium is improved.

The thickness and heat capacity of the reflecting layer is reduced while the mechanical strength and optical properties of the layer are maintained, so that recording sensitivity improves. In other words, the thermal properties and recording sensitivity of the optical recording medium can be controlled by choosing a preferable layer thickness. Since the reflecting layer utilizes the multiple interference of a laser beam, the layer can prevent deterioration and crystal growth in a high temperature and humidity environment by containing at least one element selected from the group comprising Ti, Ni, Cr, Cu, Ag, Au, Pt, Mg, Si and Mo in addition to Al.

The thin recording layer contains Te, Ge and Sb; Te, Ge, Sb and nitrogen; GeTe, Sb_2Te_3 and Sb; or GeTe, Sb_2Te_3, Sb and nitrogen. The thin recording layer is composed so that $0.2 \leqq b \leqq 0.5$ where b is the mol ratio of Sb/Sb_2Te_3. It is not preferable to have b greater than 0.5 since the erase rate declines due to the decrease in crystallization speed. When b is less than 0.2, there is a problem in that the recording amplitude of an inner circumference having a low linear velocity is reduced. By adding nitrogen to the thin recording layer, the heat conductivity of the layer is reduced. The crystallization speed of the layer is also reduced by increasing the amount of Sb. As a result, the recording sensitivity of the optical recording medium is improved.

In the MCAV recording method, the recording pulse width of the inner circumference is set larger than that of the outer circumference at 5–12 m/s linear velocity, so that heat up temperature at the inner and the outer circumferences during recording is set equal. Thus, marks of almost the same size are formed, thereby reducing mass transfer of the thin recording layer caused by overlapped marks during overwriting and improving the cycle properties of overwrite.

The total thickness of the first dielectric layer, the thin recording layer, the second dielectric layer and the reflecting layer is 250–430 nm. The 3–15 μm thick overcoat resin layer generating tensile stress is formed on the reflecting layer. As a result, tilt of the optical recording medium is almost eliminated. Tilt is an angle where the horizontal reference plane of the medium and a tangent of the surface of the medium formed with the layers intersect each other. In addition, by using a transparent substrate having a convex surface, the tilt of the optical recording medium is further minimized.

In addition, information is recorded in the MCAV recording method by varying the record starting point at the maximum of 7.7 μm within the range of 5–12 m/s linear velocity, so that the mass transfer at the thin recording layer becomes even and the cycle properties of overwrite improve.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of an optical recording medium of an embodiment of the invention.

FIG. 2(*a*) is a graph showing the correlation of the thickness of a thin recording layer, amplitude and recording power.

FIG. 2(*b*) is a graph showing the correlation between the thickness of a second dielectric layer and amplitude.

FIG. 2(*c*) is a graph showing the correlation between the thickness of a reflecting layer and the recording power.

FIG. 3 is a graph showing the tilt of an optical recording medium of one embodiment of the invention before and after an accelerated test.

FIG. 4 shows a waveform picture of an optical recording medium of one embodiment of the invention after overwriting 100,000 times.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments will be explained by referring to figures. As shown in FIG. 1, an optical recording medium of the invention consists of a transparent disk substrate 1, a first dielectric layer 2, a thin recording layer 3, a second dielectric layer 4, a reflecting layer 5 and an overcoat protective layer 6. The second dielectric layer is thinner than the first dielectric layer, and the second dielectric layer and the reflecting layer are 35–70 nm thick and 70–120 nm thick respectively, so that recording sensitivity and overwrite properties improve. The thin recording layer is 18–30 nm, and is also so thin that heat capacity can be minimized and information can be recorded with small power. Disk substrate 1 shown in FIG. 1 is a transparent resin substrate, such as a polycarbonate resin substrate, or a glass substrate. First

dielectric layer 2 formed on disk substrate 1 is made of, for example, a heat resisting mixed material of ZnS and SiO_2, and is 140–210 nm thick. Thin recording layer 3 formed on first dielectric layer 2 is made of a mixed material of GeTe, Sb_2Te_3 and Sb, and nitrogen. The layer is 18–30 nm thick. The thin recording layer is composed so that $0.2 \leq b \leq 0.5$ where b is the mol ratio of Sb/Sb_2Te_3. Sb has correlations with crystallization speed. It is not preferable to have b greater than 0.5 since the erase rate declines due to the decrease in crystallization speed. When b is less than 0.2, there is a problem in that the recording amplitude of an inner circumference having a low linear velocity is reduced. Second dielectric layer 4 formed on thin recording layer 3 is made of the same material used for first dielectric layer 2, and is 35–70 nm thick. Reflecting layer 5 formed on second dielectric layer 4 utilizes the multiple interference of a laser beam, and is mainly made of Al. The thickness of the reflecting layer is 70–120 nm. When only Al is used for the reflecting layer, crystal grain size in the layer grows under a high temperature and humidity environment, so that the quality of the layer deteriorates due to intergranular corrosion. Thus, besides Al, at least one element selected from the group comprising Ti, Ni, Cr, Cu, Ag, Au, Pt, Mg, Si and Mo is added to the layer so as to prevent crystal growth and deterioration under the above environment. Overcoat resin protective layer 6 formed on reflective layer 5 cures and shrinks, thus generating tensile stress. The layer is made of ultraviolet ray curing resin, and is formed by a spin coat method at a thickness of 3–15 μm. A vacuum evaporation method or a sputtering method is applied to form first dielectric layer 2, second dielectric layer 4, thin recording layer 3 and reflecting layer 5.

When a 35 mW semiconductor laser is used so as to record on a phase change optical disk, the maximum output of the disk is 14 mW with 40% transmission efficiency of optical pickup. In consideration of the unevenness of optical pickup, it is necessary for a disk to record at 12 mW or less. In order to improve reloading properties by increasing the recording sensitivity of a disk, not only optical properties but also thermal properties and mechanical strength have to be considered.

The reasons for specifying the range of layer thickness are explained below.

(1) The thickness of the first dielectric layer 2 will now be explained. The thicknesses of thin recording layer 3, second dielectric layer 4 and reflecting layer 5 were fixed, and the thickness of first dielectric layer 2 was varied. Within the range of 140–210 nm thickness, the absorption Ad of crystal with optical characteristic, the absorption Aw of an amorphous state, and the difference in reflectance (ΔR) of crystal showing a signal size and the amorphous state almost stayed the same. Recording power (C/N ratio>50 dB power) was also the same. When the thickness was outside the range, there was a problem in that ΔR and signal amplitude became small.

(2) The thickness of the thin recording layer 3 will now be explained. FIG. 2(*a*) is a graph showing recording power when the thicknesses of the first dielectric layer 2, the second dielectric layer 4 and the reflecting layer 5 are fixed at 170 nm, 40 nm and 70 nm respectively and the thickness of the thin recording layer is varied. According to the graph, when the recording power is 12 mW or less and amplitude is within ±2 db, the thickness of thin recording layer 3 is 18–30 nm. When the thickness is more than 30 nm, heat capacity becomes large and sensitivity lowers. The amplitude becomes small when the thickness is less than 18 nm, thus providing an undesirable result.

(3) The thickness of the second dielectric layer 4 will now be explained. The thickness of the layer has to be determined in consideration of optical properties and thermal cooling speed. FIG. 2(*b*) is a graph showing the correlation between recording power and signal amplitude when the thicknesses of the first dielectric layer 2, the thin recording layer 3 and the reflecting layer are fixed at 170 nm, 23 nm and 70 nm respectively and the thickness of the second dielectric layer 4 is varied. The signal amplitudes from using 70 nm or less thickness of second dielectric layer 4 are within −3 dB of the amplitude with 30 nm thickness. When the thickness is more than 70 nm, the signal amplitudes are undesirably small. The recording power is 12 mW or less when the thickness is 30 nm or more. Recording thin layer 3 becomes close to reflecting layer 5 when the thickness of the second dielectric layer is less than 30 nm. Thus, more heat is likely to disperse and sensitivity declines, thus providing undesirable results.

(4) The thickness of the reflecting layer 5 will now be explained. The thickness of the layer has to be decided in consideration of heat capacity and mechanical strength. FIG. 2(*c*) is a graph showing recording power when the thicknesses of first dielectric layer 2, thin recording layer 3 and second dielectric layer 4 are fixed at 170 nm, 23 nm and 40 nm respectively, and the thickness of the reflecting layer is varied. When the reflecting layer is 120 nm or less thick, recording sensitivity with 12 mW or less recording power is obtained. Recording power is 9 mW and constant when the thickness is 70 nm or less. The experiment of overwrite cycle properties was directed to disks of various reflecting layer thickness. In the experiment, random signals. modulated to "2–7" modulation by PPM (Pit Position Modulation) recording, were used. At 5 m/s linear velocity, 4.03 MHz was employed as the maximum recording frequency, and 8.87 MHz was used as the maximum recording frequency at 12 m/s linear velocity. The wavelength of the semiconductor laser was 780 nm, and NA (Numerical Aperture) was 0.5. Jitter, gaps between signals to be recorded and recorded signals, was measured by a time interval analyzer. As a result, when the thickness was less than 60 nm, it was found that the mechanical strength of the reflecting layer was weak. With 60 nm or more thickness, the layer had 100,000 or more overwrites. Therefore, the thickness of the reflecting layer is preferably 70–100 nm.

If the mixed ratio of SiO_2 in ZnS-SiO_2 constituting first and second dielectric layers 2 and 4 is 5 mol % or less, the effect of minimizing crystal grain size is reduced. When the ratio is 40 mol % or more, the strength of SiO_2 becomes insufficient. Thus, is preferable that the mole fraction of SiO_2 is 5–40 mol %.

Moreover, the temperature at the inner and the outer circumferences during recording is the same since the recording pulse width of the inner circumference is set larger than that of the outer circumference. Thus, the sizes of recording marks become almost the same at the inner and the outer circumferences, thus minimizing mass transfer at the thin recording layer, caused by overlapping marks, and signal deterioration. It is preferable that the pulse width of the inner circumference is 40–60 ns and that of the outer circumference, 30–40 ns. Within these ranges of pulse width and within the range of 5–12 m/s for the inner and the outer circumferences, an overwrite experiment was carried out. The deterioration of jitter at 100,000 or more overwrites was not found. Thus, the ratio of pulse width of the inner circumference relative to that of the outer circumference is 1.2 or more.

In the invention, first and second dielectric layer 2 and 4 made of ZnS and SiO_2, thin recording layer 3 comprising Te,

Ge, Sb and nitrogen and reflecting layer 5 made mainly of Al are formed on a 1.2 mm thick substrate having a 120nm disk diameter. The total thickness of these four layers is 430 nm or less. When the layers are formed on a signaling surface of the disk substrate, the surface protrudes, thus generating compressive stress and about 3 mrad tilt. Therefore, by forming 3–15 μm thick overcoat resin protective layer 6 generating tensile stress on the reflective layer, the compressive stress is offset. As a result, an optical disk having little tilt is provided with only about 1–2 mrad even on the outer circumference. Overcoat resin protective layer 6 cannot offset the compressive stress if its thickness is less than 3 μm because the strength of the layer is not sufficient. On the other hand, when the layer is more than 15 μm thick, its tensile stress is so large that the surface of the optical disk where the layers are formed becomes concave and the tilt of the disk becomes large. Thus, the thickness of overcoat resin protective layer 6 is preferably 3–15 μm. A mixed material of acrylic ultraviolet ray curing resin, such as urethane acrylate, and acrylic ester monomer is used for overcoat resin protective layer 6. However, the material for the layer is not limited to this alone. The above-mentioned properties can be provided as long as the material for the layer has about 10 percentage of contraction by curing.

A substrate is molded beforehand to have a convex surface with 1–2 mrad tilt (surface to be recorded with information) relative to an inner circumference reference plane. Then, first dielectric layer 2, thin recording layer 3, second dielectric layer 4 and reflecting layer 5 are formed on the surface. The total thickness of the four layers is 430 nm or less, and the compressive stress of the layers is 0.5×10^9 dyn/cm^2 or less. Ultraviolet ray curing resin is formed on reflecting layer 5 at 3–15 μm thickness as overcoat protective layer 6 for generating tensile stress, thus decreasing tilt. After forming the overcoat protective layer on the four layers, the substrate and the layers are annealed at 100° C. for one hour, so that the stresses of the substrate, the thin layers, and the overcoat protective layer are relaxed during the forming step. Moreover, the substrate and the layers will not be deformed. As a result, the negative effect on recording properties caused by tilt such as off-tracking can be minimized. The above-noted substrate, which has a concave surface with 1–2 mrad (surface to be recorded with information) relative to an inner circumference reference plane, can be easily prepared by means of changing the temperature distribution of a metallic mold by an injection method. In the above-mentioned method, the tilt of a disk can be set to less than 5 mrad. The disk prepared in the method described above was placed in an environment of 80% humidity and 90° for 20 hours (accelerated test), and then was removed. The disk was left to sit at room temperature, and its tilt was measured. The surface of the disk formed with layers warped significantly into a convex shape for several hours after removal. However, after 48 hours, the tilt became less than 5 mrad even though the tilt of the outer circumference was slightly greater than the tilt before the accelerated test (FIG. 3). The tilt was measured by an optical disk tester: LM-110 (manufactured by Ono Sokki Co., LTD, Japan).

At the 5–12 m/s linear velocity of the MCAV recording method, which records by changing recording frequencies in accordance with linear velocity, information is recorded within a range where the information is stored in a sector by changing a record starting point, and is overwritten evenly in the sector. Thus, mass transfer that is generated by recording new marks over previously recorded marks becomes even. As a result, the optical recording medium of the invention prevents the phenomenon whereby recording layers shift to a section and acculmulate where the same signals are always recorded such as a resync section, lowering recording sensitivity. This effect of the invention is significant at a low power side where the overlap of marks is small, so that the power margins of overwrite properties increase. When the record starting point was changed at the maximum of 7.75 μm and was shifted by a 0.484 μm interval, no deterioration was found after overwriting 100,000 times, as shown in FIG. 4, and the effect was significant.

The invention is explained in further detail in the following example.

EXAMPLE 1

On one surface of a 1.2 mm thick polycarbonate substrate 120 mm in diameter, a 170 nm thick dielectric layer was formed of a mixed material of ZnS and SiO_2 that contained SiO_2 at 20 mol %. A 26 nm thick recording layer made of a material of $Te_{53.0}Ge_{22.6}Sb_{24.4}$ (Te:53.0 atoms %, Ge:22.6 atom % and Sb:24.4 atom %)) mixed with nitrogen was formed on the first dielectric layer. On the recording layer, a 44 nm thick second dielectric layer was formed of the same material as the material used for the first dielectric layer. A 95 nm thick reflecting layer made of Al alloy was formed on the second dielectric layer by a sputtering method. The high frequency sputtering method was applied to form the first and the second dielectric layers with 2 mTorr sputtering pressure and by using Ar gas (30SCCM). The direct current sputtering method was applied to form the recording layer with 1 mTorr sputtering pressure and by using a mixed gas of Ar (15SCCM) and N_2 (0.8SCCM). The reflecting layer was formed by the direct current sputtering method with 2 mTorr sputtering pressure and Ar gas (15SCCM). In order to protect the four layers, acrylic ultraviolet curing resin, such as SD101 (manufactured by DAINIPPON INK & CHEMICALS, Japan) which is a mixed material of urethane acrylate and acrylic ester monomer, was coated on the reflecting layer to 5 μm thickness by a spin coat wave, thus preparing a single plate structure disk. The tilt of the disk was measured by an optical disk tester (LM110 manufactured by Ono Sokki Co., LTD, Japan), and was 3 mrad. The recording and erasing properties of the disk were measured by an optical disk drive having 2026 rpm, a 780 nm semiconductor laser wavelength and 0.5 NA. At the outermost circumference with 12 m/s linear velocity, signals at 8.87 MHz recording frequency were recorded with 32 ns pulse width. The C/N ratio was measured by a spectrum analyzer and was 50 dB or more. The build-up power of the C/N ratio was 12 mW. 3.32 MHz signals were overwritten after 8.87 MHz signals were recorded, so that the erase ratio was obtained by subtracting spectrum in the process of overwriting 3.32 MHz signals from spectrum in the process of recording 8.87 MHz signals: this was 25 dB.

The cycle properties of overwrite were tested. Random signals modulated to "2–7" by PPm recording were used to test overwrite.

The method of recording by changing a record starting point within a range of keeping recording information in a sector was applied. The record starting point was changed by 7.75 μm at maximum, and was randomly shifted at an interval of 0.484 μm within a range.

At the inner circumference with 5 m/s linear velocity, 4 MHz was applied as the highest recording frequency. 8.87 MHz was used as the highest frequency at the outer circumference with 12 m/s linear velocity. Jitter was measured by a time interval analyzer. According to the measurement, no

deterioration was found from the beginning to 100,000 or more overwrites at 5 m/s and 12 m/s linear velocity.

EXAMPLE 2

The following table shows the change in recording sensitivity and overwrite properties of a disk when the thicknesses of the first and the second dielectric layers and of the reflecting layer are changed. The layers were formed by the method applied in Example 1.

	Condition			Results	
Sample No.	* (nm)	** (nm)	*** (nm)	Recording sensitivity	Overwrite
1	230	30	95	X	Δ
2	210	35	95	Δ	O
3	170	43	95	O	O
4	140	50	95	O	O
5	130	55	95	O	X
6	170	62	95	O	O
7	150	70	95	Δ	O
8	160	75	95	Δ	X
9	170	43	60	O	X
10	140	53	70	O	O
11	190	53	80	O	O
12	150	53	90	O	O
13	130	53	100	O	X
14	210	53	110	O	O
15	140	53	120	O	O
16	170	53	130	X	O
17	48	53	95	X	X
18	40	53	95	X	X
19	35	53	95	X	X

*Thickness of first dielectric layer
**Thickness of second dielectric layer
***Thickness of reflecting layer
O: Good, Δ: Fair, X: Poor

As has been shown the optical recording medium has high recording sensitivity and excellent repeated recording and deleting properties.

The invention may be embodied in other forms without departing from the spirit or essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not restrictive, the scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

What is claimed is:

1. A method of using an optical recording medium, comprising:
   (a) providing an optical recording medium comprising:
      (i) a transparent substrate having two surfaces,
      (ii) a first dielectric layer formed on one surface of said transparent substrate,
      (iii) a recording layer formed on said first dielectric layer,
      (iv) a second dielectric layer formed on said recording layer, said second dielectric layer being thinner than said first dielectric layer and being 35–70 nm thick, and

      (v) a reflecting layer formed on said second dielectric layer, said reflecting layer being 70–120 nm thick; wherein said recording layer has properties of becoming amorphous after its temperature is increased, then melting and quenching by absorbing energy from the irradiation of a laser beam, and of crystallizing its amorphous state by a temperature rise; and
   (b) recording information by a Modified Constant Angular Velocity recording method which comprises changing recording frequencies in accordance with linear velocity; wherein:
      (i) said linear velocity is in the range of 5–12 m/s;
      (ii) an inner circumference recording pulse width is larger than an outer circumference recording pulse width, and
      (iii) a ratio of said inner circumference recording pulse width to said outer circumference recording pulse width is 1.2 or more.

2. The method as in claim 1, wherein the recording pulse width is 40–60 ns at 5 m/s linear velocity and is 30–40 ns at 12 m/s linear velocity.

3. The method as in claim 1, the Modified Constant Angular Velocity recording method is applied so as to record information by changing a record starting point at the maximum of 7.75 μm within 5–12 m/s linear velocity.

4. The method as in claim 1, wherein the thin recording layer is 18–30 nm thick.

5. The method as in claim 1, wherein the first dielectric layer is 140–210 nm thick.

6. The method as in claim 1, wherein the first dielectric layer comprises a mixed material of ZnS and SiO_2; wherein the second dielectric layer comprises a mixed material of ZnS and SiO_2; and wherein said mixed material comprises SiO_2 at 5–40 mol % and ZnS at 60–95 mol %.

7. The method as in claim 1, wherein the reflecting layer comprises Al as a main material and at least one metal selected from the group consisting of Ti, Ni, Cr, Cu, Ag, Au, Pt, Mg, Si and Mo.

8. The method as in claim 1, wherein the recording layer comprises Te, Ge and Sb.

9. The method as in claim 8, wherein the recording layer further comprises nitrogen.

10. The method as in claim 1, wherein the recording layer comprises GeTe, Sb_2Te_3, Sb and nitrogen.

11. The method as in claim 10, wherein the recording layer is composed so that $0.2 \leq b \leq 0.5$ where the mol ratio of Sb/Sb_2Te_3 is b.

12. The method as in claim 1, wherein the optical recording medium further comprises a 3–15 μm thick overcoat resin protective layer on the reflecting layer; said overcoat resin protective layer generating tensile stress.

* * * * *

Appendix C

US005102709A

United States Patent [19]

Tachibana et al.

[11] **Patent Number: 5,102,709**

[45] **Date of Patent: Apr. 7, 1992**

[54] **OPTICAL RECORDING MEDIUM AND PROCESS FOR PRODUCTION THEREOF**

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[73] Assignee: **Canon Kabushiki Kaisha**, Tokyo, Japan

[21] Appl. No.: **514,289**

[22] Filed: **Apr. 25, 1990**

[30] **Foreign Application Priority Data**

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May 2, 1989 [JP] Japan 1-113317

[51] **Int. Cl.**[5] **B32B 3/02**

[52] **U.S. Cl.** .... **428/64**; 428/65; 428/76; 428/423.1; 428/688; 428/913; 369/288; 346/76 L; 346/135.1; 430/945; 427/162; 427/166; 427/167

[58] **Field of Search** .... 428/64, 65, 76, 423.1, 428/688, 913; 369/288; 346/76 L, 135.1; 430/945; 427/162, 166, 167

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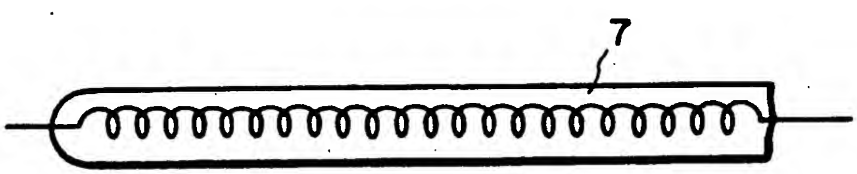
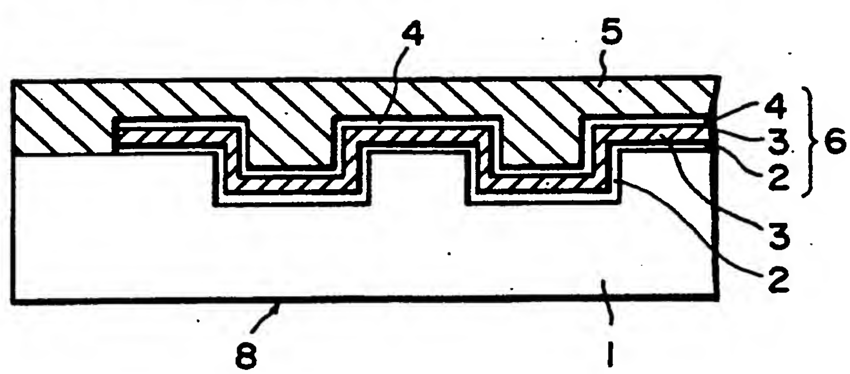
Primary Examiner—Patrick J. Ryan
Attorney, Agent, or Firm—Fitzpatrick, Cella, Harper & Scinto

[57] **ABSTRACT**

An optical recording medium is formed to include a resinous substrate, a laminate film including an inorganic dielectric layer and a recording layer, and a resinous protective film, respectively disposed on the substrate. The laminate film is formed to have a compression stress of 15–55 kg/mm² so as to be in a dense film free from cracking or peeling. The resinous protective layer is formed to have a tensile stress of 2.5–5.5 kg/mm² so as to compensate the compression stress in the laminate film, thus preventing warp and skew of the optical recording medium. The resinous protective film may preferably be formed from a photocurable composition comprising an increased amount of a polyacrylate compound providing a dense film and a urethane acrylate compound providing a flexibility.

22 Claims, 2 Drawing Sheets





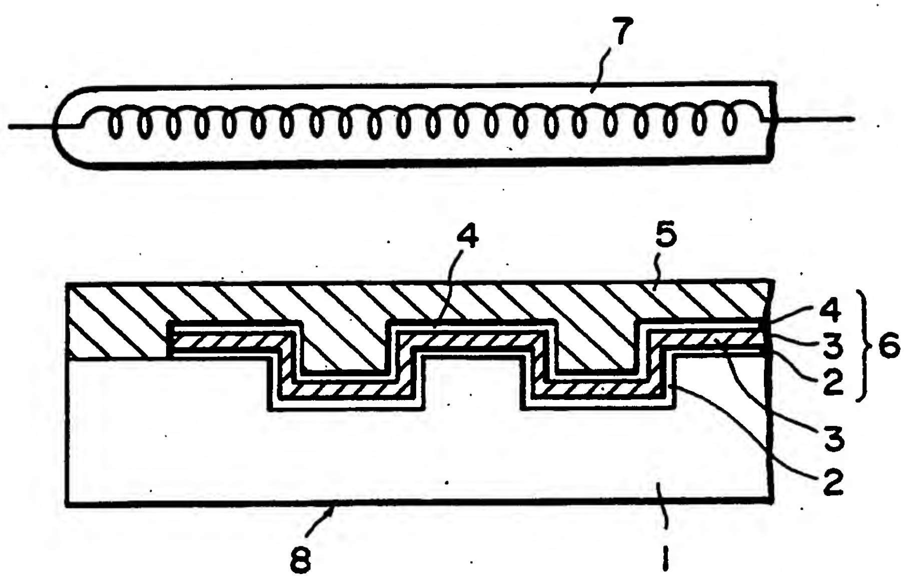


FIG. 1

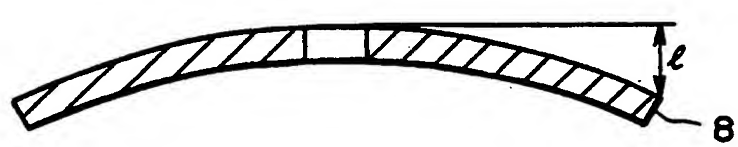


FIG. 2

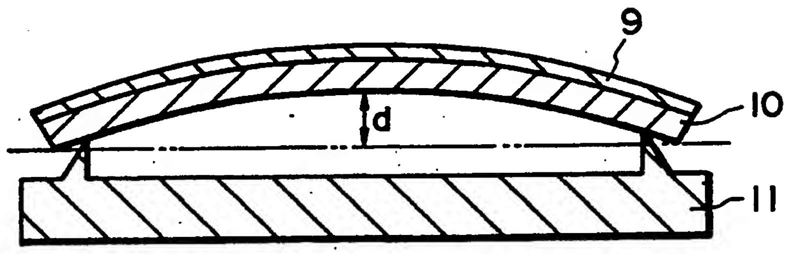


FIG. 3

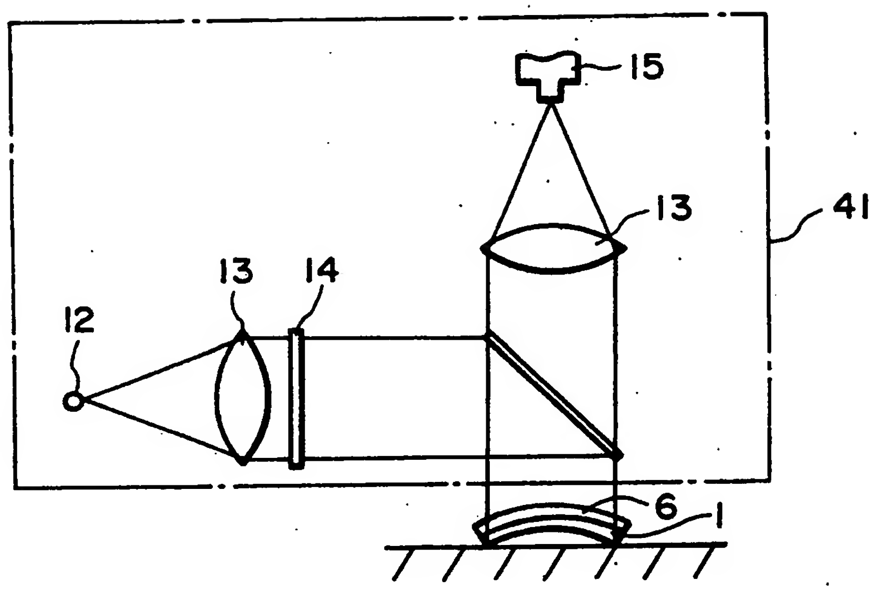


FIG. 4

OPTICAL RECORDING MEDIUM AND PROCESS FOR PRODUCTION THEREOF

FIELD OF THE INVENTION AND RELATED ART

The present invention relates to an optical recording medium capable of recording, reproduction and/or erasure of data with a light beam and a process for producing the same.

Hitherto, as an optical recording medium for recording or reproducing data with light, there has been known a recording material comprising a recording layer formed on a substrate and sandwiched between stabilizing layers comprising an inorganic dielectric for preventing deterioration of the recording layer by oxidation, which is further covered with a transparent protective layer (U.S. Pat. No. 4,370,391 corr. to Japanese Laid-Open Patent Application JP-A-56-130393). Such a protective layer has been composed of an inorganic compound such as SiO_2. The protective layer is required to be as thick as several microns for surface protection. However, such a thick layer of an inorganic compound such as SiO_2 is brittle and is liable to crack spontaneously. For this reason, a resinous protective layer has been proposed including, e.g., one of a photopolymerizable organic substance, such as an acrylate-type resinous composition (JP-A-61-123593).

However, when such a resinous protective layer is applied to an optical recording medium of a structure as described above, the recording medium is caused to have large initial warp and/or skew due to a laree stress in the stabilization layer of an inorganic dielectric, which warp and/or skew can be enhanced under an environmental durability test (e.g., by standing for 2000 hours under 80° C. and 90% R.H.), so that it becomes impossible to load an evaluating apparatus with the recording medium, thus failing in recording, reproduction or erasure, in some cases. More specifically, the optical recording medium is deformed to be convex on the side of the laminate film due to a stress in the laminate film.

In case where the recording layer and inorganic dielectric protective layer are formed while suppressing a temperature increase of the substrate to minimize the stress in the resultant laminate film, the warp and skew can be decreased but the deterioration of the laminate film, such as occurrence of cracks in or peeling of the inorganic dielectric film, is liable to occur and the oxidation or corrosion of the recording layer is developed from the resultant defects to cause difficulties, such as an increase in bit error rate (B.E.R.) and deterioration of C/N value.

Herein, the warp refers to a deformation of the optical recording medium in the radial direction, and the skew refers to a deformation of the optical recording medium in the circumferential direction.

Heretofore, for the purpose of preventing the warp of the medium, a pair of identical structures having opposite recording layers have been applied to each other to provide a double-sided disk, or a medium is applied with an adhesive onto a rigid protective substrate as disclosed in JP-A-60-10431.

In recent years, however, a thinner and lighter medium has been required, so that a single-sided no-adhesive medium having no rigid substrate applied thereto but having only a resinous protective layer on the recording layer has been proposed, but it has been very difficult to obtain such a single-sided no-adhesive medium free of warp.

Thus, there has been known a single-sided no-adhesive optical recording medium comprising an inorganic dielectric layer, a recording layer and a resinous protective layer disposed on a substrate and free from further application of a rigid substrate, but no single-sided no-adhesive medium has been free from warp before the present invention.

SUMMARY OF THE INVENTION

In view of the above problems, an object of the present invention is to provide an optical recording medium having a minimized warp or skew which does not increase even after an environmental durability test.

Another object of the present invention is to provide an optical recording medium having a minimized bit error rate (B.E.R.) and a C/N value which does not deteriorate and ensures a reliability for a long term.

According to an aspect of the present invention, there is provided an optical recording medium comprising: a resinous substrate, a laminate film including an inorganic dielectric layer and a recording layer, and a resinous protective film, disposed on the substrate; wherein the resinous protective layer has a tensile stress of 2.5–5.5 kg/mm^2, and the laminate film has a compression stress of 15–55 kg/mm^2.

According to another aspect of the present invention, there is provided an optical recording medium, comprising: a resinous substrate, a laminate film including an inorganic dielectric layer and a recording layer, and a resinous protective film, disposed on the substrate; wherein the resinous protective layer comprises a cured film of a photocurable resin comprising 60 wt. % or more of a polyfunctional acrylate compound having 5 or more functional groups and 10 wt. % or less of a urethane acrylate compound.

According to a further aspect of the present invention, there is provided a process for producing an optical recording medium, comprising:

coating resinous substrate with a laminate film including an inorganic dielectric layer and a recording layer so as to provide the laminate film with a compression stress of 15–55 kg/mm^2, and

coating the laminate film with a resinous protective layer so as to provide the resinous protective layer with a tensile stress of 2.5–5.5 kg/mm^2.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic sectional view of an embodiment of the optical recording medium according to the present invention.

FIG. 2 is a schematic sectional view illustrating a warp of an optical recording medium.

FIG. 3 is a schematic sectional view for illustrating a method of measuring a stress in a resinous protective film.

FIG. 4 is a view for illustrating a method of measuring a stress in a laminate film.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows an embodiment of the optical recording medium according to the present invention. Referring to FIG. 1, an optical recording medium 8 has a laminated structure comprising a resinous substrate 1, inorganic dielectric layers 2 and 4, a recording layer 3, and a resinous protective layer 5, wherein the recording layer 3 and inorganic dielectric layers 2 and 4 in combination constitute a laminate film 6.

The (compression) stress in the laminate film 6 according to the present invention may preferably be in the range of 15-55 kg/mm^2, particularly 20-50 kg/mm^2 in view of the stability of the recording layer. If the laminate film 6 has a stress below 15 kg/mm^2, the laminate film, particularly the inorganic dielectric layer therein is liable to cause cracking or peeling, and if the stress exceeds 55 kg/mm^2, the optical recording medium causes a large degree of warp and skew to result in cracking or peeling of the laminate film. Further, in case of an optomagnetic recording medium, a laminate film thickness in the above range provides a large magneto-optical Kerr rotation angle to result in a good S/N of detection signal.

The resinous protective film 5 according to the present invention may have a tensile stress of 2.5-5.5 kg/mm^2, preferably 3-5 kg/mm^2 for prevention of warp. A stress in the resinous protective film 5 in the above range provides a good balance with the stress in the laminate film 6 to provide an optical recording medium with little deformation.

In the present invention, the recording layer 3 may preferably comprise an inorganic material, examples of which may include amorphous magnetic recording materials, such as TbCO, GdTeCO, GdFeCO and GdTbFeCo; Bi, Al; calcogenides comprising Se, Te, etc.; and alloys of these. The recording layer can have a laminate structure of these materials. The recording layer may preferably have a thickness of 200-1000 Å, particularly 500-900 Å. Further, in the present invention, the recording layer can constitute a reflection layer for a readout beam for reproducing data recorded in advance, which is not used for writing data therein.

The inorganic dielectric layers 2 and 4 may preferably comprise Si_3N_4, SiO_x, ZnS, SiC, etc., among which Si_3N_4 is particularly preferred. The inorganic dielectric layer is formed on at least one side of the recording layer 3 but is preferably formed on both sides of the recording layer in order to sufficiently protect the recording layer.

The inorganic dielectric layer may preferably have a thickness of 100-1000 Å, further preferably 400-1000 Å, particularly 450-750 Å.

The layers in the laminate film 6 may preferably be formed by vapor deposition, such as vacuum evaporation or sputtering, so as to provide a uniform film, and sputtering is particularly preferred since the stress in these layers can be easily controlled. The stress in the laminate film 6 can be adjusted by controlling the film-forming conditions of the respective layers including the inorganic dielectric layer(s) and recording layer, inclusive of sputtering pressure, input power and disposition of target in case of sputtering, and further control of N_2 partial pressure. More specifically, in case of forming a laminate film composed of inorganic dielectric layer/recording layer/inorganic dielectric layer comprising 650 Å-thick Si_3N_4 layer/400 Å-thick Gd-Tb amorphous recording layer and 400 Å-thick Tb-Fe amorphous recording layer/700 Å-thick Si_3N_4 layer by sputtering, the first Si_3N_4 layer may be formed under a sputtering pressure of 0.1-0.3 Pa and an input power of 500-1500 W, the recording layer may be formed under 0.2-0.5 Pa and 500-1500 W, and the second Si_3N_4 layer may be formed under 0.1-0.3 Pa and 500-1500 W to provide a laminate film with a compression stress of 15-55 kg/mm^2.

In the present invention, it is also possible to form a reflecting film of, e.g., Al, on the laminate film including the inorganic dielectric layer and recording layer so as to improve the C/N value.

The resinous protective film may suitably be formed from a resin providing its cured film with a tensile stress of 2.5-5.5 kg/mm^2, which may be thermosetting resin, photo-curable resin and electron beam-curable resin. From the viewpoint of providing a protective film capable of preventing transmission of oxygen and moisture and having an appropriate tensile stress, photo- or ultraviolet-curable or electron beam-curable resin may suitably be used. The ultraviolet-curable resin may suitably be an acrylate-type resin composition or a photopolymerizable epoxy resin, particularly an acrylate-type resin composition for easy adjustment of the stress. The ultraviolet-curable acrylate-type resin may suitably comprise (A) a prepolymer component, (B) a reactive diluent component, and (C) a photopolymerization initiator, wherein the components (A) and (B) are mixed in proportions of 0-100 wt. %, preferably, 5-95 wt. % and 100-0 wt. %, preferably, 95-5 wt. %, respectively, and the component (C) is preferably contained in a proportion of 0.1-10 wt. %. Examples of the component (A) may include polyester acrylate, urethane acrylate, and epoxy acrylate. The component (B) may suitably be a mono-functional monomer or a polyfunctional monomer, such as an acrylic acid ester of a polyhydric alcohol. The component (C) may be ay known photopolymerization initiator but may preferably be one providing a composition with a good storage stability, examples of which may include initiators of benzoin alkyl ether-type, acetophenone-type, propiophenone-type, anthraquinone-type, and thioxanthone-type. These initiators may be used singly or in a mixture of two or more species in any proportions.

In the present invention, an ultraviolet-curable acrylate-type resin composition providing a cured film with a tensile stress of 2.5-5.5 kg/mm^2 may be selected from those described above.

A preferred class of the acrylate-type resin composition may be formed as a mixture comprising 60 wt. % or more of a polyfunctional acrylate compound having 5 or more functional groups (i.e., acrylate groups) as a component (B) and 10 wt. % or less of a urethane acrylate compound as a component (A). The resin composition provides a dense protective layer having a high degree of crosslinking and thus having a high tensile stress and small moisture absorptivity and permeability through polymerization under irradiation with light or electron beam because it contains 60 wt. % or more of the polyfunctional acrylate compound, and also provides the protective film with a sufficient flexibility free from cracking, etc., while retaining a high stress, because it contains 10 wt. % or less of the urethane acrylate compound so as to compensate for a decrease in flexibility of the protective film caused by the increased content of the polyfunctional acrylate compound. Further, the resultant resinous protective film has a high gel

content and contains little non-reacted monomer, so that corrosion or pitting of the recording layer due to such non-reacted monomer can be suppressed to provide an optical recording medium having minimized skew or warp, a decreased B.E.R., little degradability in C/N value and thus having a particularly excellent long-term reliability.

The urethane acrylate compound is free from remaining of acrylic acid at the time of curing and has a small moisture-absorptivity and a large heat resistance compared with other flexibility imparting compounds, such as epoxy acrylate, polyester acrylate and polyether acrylates, so that it is particularly suitably used in the resinous protective layer according to the present invention.

In the resinous protective layer, the polyfunctional acrylate compound having 5 or more functional groups may preferably constitute 60 wt. % or more, particularly 75 wt. % or more, further preferably 85 wt. % or more, of the components constituting the resinous protective layer. Further, the urethane acrylate compound may preferably constitute 10 wt. % or less, particularly 2-8 wt. %, of the components constituting the protective layer.

Examples of the polyfunctional acrylate compound having 5 or more functional groups may include: dipentaerythritol hexaacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexamethacrylate, dipentaerythritol hexa(ω-acryloyloxy-ϵ-caproate), and dipentaerythritol hexa(ω-methacryloyloxy-ϵ-caproate). These compounds may be used singly or in mixture. Among these, dipentaerythritol hexaacrylate is particularly preferred in respect of providing a high stress and a high degree of crosslinking.

The urethane acrylate compound may be prepared by urethanation between an addition condensation product of a carbonate diol (average molecular weight=500-5000) and ϵ-caprolactone (I) and an organic polyisocyanate (II), followed by acrylate formation by reaction with a hydroxyacrylate compound (III).

The carbonate diol giving the urethane acrylate compound according to the present invention may for example be prepared through transesterification between (a) a carbonate derivative which may be selected from a class including diaryl carbonates or dialkyl carbonates, such as diphenyl carbonate, bischlorophenyl carbonate, dinaphthyl carbonate, phenyl tolyl carbonate, phenyl chlorophenyl carbonate, 2-tolyl 4-tolyl carbonate, dimethyl carbonate and diethyl carbonate, and (b) a diol or a polyester diol which may be selected from diols, such as 1,6-hexanediol, neopentyl glycol, 1,4-butanediol, 1,8-octanediol, 1,4-bis(hydroxymethyl)cyclohexane, 2-methylpropanediol, dipropylene glycol and dibutylene glycol, or polyester diols obtained by reacting the diols with dicarboxylic acids, such as oxalic acid, malonic acid, succinic acid, adipic acid, azelaic acid, and hexahydrophthalic acid.

The thus obtained carbonate diol may be a monocarbonate diol having one carbonate structure in its molecule or a polycarbonate diol having two or more carbonate structures in its molecule. Commercially available examples of the carbonate diol may include: Desmophen 2020E (mfd. by Sumitomo Bayer K.K.), DN-980 (Nihon Polyurethane K.K.), DN-981 (Nihon Polyurethane K.K.), and DN-983 (Nihon Polyurethane K.K.).

The reaction between the carbonate diol and the ϵ-caprolactone may preferably be effected in the presence of a catalyst in a catalytically effective amount, which may preferably be 0.001-1.0 wt. %, particularly 0.01-0.2 wt. %, of the ϵ-caprolactone. Examples of the catalyst effective for the reaction may include: organic titanium compounds, such as tetraisopropyl titanate and tetrabutyl titanate, and tin compounds, such as tetraphenyltin and tetraoctyltin. The reaction between the carbonate diol and the ϵ-caprolactone may be initiated at a temperature of 110°-200° C. and continued for a time sufficient for the completion of the reaction. The ϵcaprolactone may preferably be used in an amount of 1-5 mols per mol of the carbonate diol.

In order to minimize oxidation as a side reaction, the reaction may preferably be effected in an inert gas atmosphere of nitrogen, etc. The reaction mixture including the addition condensation product thus obtained can be used as it is in a subsequent reaction.

The urethane acrylate compound in the present invention may preferably contain averagely 1-5 mols of ϵ-caprolactone added thereto.

Next, examples of the organic polyisocyanate (II) may include isophorone diisocyanate, hexamethylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate, diphenylmethane-4,4'-diisocyanate, lysine diisocyanate, and dimer acid diisocyanate. The urethane formation reaction between the addition condensation product (I) and the organic polyisocyanate (II) may preferably be effected at 50°-80° C.

Examples of the hydroxyacrylate compound (III) may include hydroxyethyl acrylate and hydroxypropyl acrylate. In the acrylate formation reaction, a hydroxyacrylate compound may be used in a stichiometric amount or a small excess thereof for acrylating the terminal isocyanate group resultant in the above urethanation. The reaction may be effected in the presence of a known catalyst, such as a tertiary amine, dibutyltin dilaurate or dioctyltin dilaurate in order to promote the reaction between the isocyanate group and the hydroxyl group. In order to prevent gel formation due to radical polymerization during the reaction, it is preferred to add a polymerization inhibitor, such as hydroquione, hydroquinone monomethyl ether, methylhydroquinone, p-benzoquinone or phenothiazine in a proportion of 50-2000 ppm in advance of the reaction. The reaction temperature may preferably be 60°-90° C.

The resin composition for providing the resinous protective layer according to the present invention may preferably contain a photopolymerization initiator in addition to the above components (A) and (B).

The photopolymerization initiator may be selected from a wide scope of compounds which can absorb ultraviolet rays to generate radicals. Representative examples thereof may include acetophenones, such as p-tert-butyltrichloroacetophenone, 2,2'-diethoxyacetophenone and 2-hydroxy-2-methyl-1- phenylpropane-1-one; ketones, such as benzophenone, Michler's ketone, 2-chlorothioxanthone, and 2isopropylthioxanthone; benzoin and benzoin ethers, such as benzoin isopropyl ether; and benzil and benzil ketals, such as benzil dimethyl ketal, and hydroxycyclohexyl phenyl ketone.

These photopolymerization initiators may be used singly or in mixture of two or more species. The photopolymerization initiator may preferably be added in a proportion of 0.1-10 wt. %, particularly 1-5 wt. %.

The composition for the resinous protective layer can further contain other additives, such as silane coupling agent, polymerization inhibitor, and leveling agent.

These additives may be added in a proportion of 0–5 wt. %, respectively, of the composition.

In addition to the above polyfunctional compound and the urethane acrylate compound as preferred components, the photo-curable composition can further contain other compounds selected from the above components (A) and (B), a preferred example of which may be a polymerizable monomer having four or less functional groups, such as TMPTA (trimethylolpropane triacrylate and MANDA (neopentyl hydroxypivalate diacrylate). The addition amount thereof should preferably be suppressed in the range of 0–30 wt. %, particularly 0–15 wt. %, so as to prevent corrosion and warp of the laminate film.

The resinous protective layer in the optical recording medium according to the present invention may preferably have a thickness of 2–20 microns, particularly 5–15 microns. Above 20 microns, the resinous protective layer is liable to peel due to curing shrinkage. On the other hand, below 2 microns, the laminate film 6 cannot be sufficiently protected from external damage.

The resinous protective layer according to the present invention may be formed by application of the composition by means of a spin coater, a roller coater, a bar coater, etc., followed by irradiation with ultraviolet rays or electron beam for curing.

The resinous substrate **1** may be composed of acrylic resin, polycarbonate resin, polystyrene resin, polyolefin resin. The substrate may preferably have a thickness free from difficulty in recording and/or . reproduction due to dust attached to the surface thereof, for example, 0.3-5 mm, particularly about 0.8–1.5 mm.

A pair of the optical recording media according to the invention can be applied to each other with an adhesive disposed between the resinous protective layers so as to dispose the resin substrates on the outer sides, thus forming a double-sided medium. However, the medium according to the present invention is particularly effectively used as a single-sided optical recording medium which is liable to warp.

It is possible to include particles of alumina, zirconia, SiN, SiO_2, TiO_2, etc., as a filler in the resinous protective layer. The surface smoothness of the resinous protective layer can be improved by inclusion of such particles, so that it becomes possible to prevent crush of a magnetic head in an optical recording medium of the magnetic field-modulated overwrite-type having an amorphous magnetic recording layer and using a floating type magnetic head.

As described above, according to the present invention, there is provided an optical recording medium which is free from cracking or peeling of the laminate film, has a minimized warp or skew and accordingly has suppressed the occurrence of errors in the recording, reproduction and erasure.

Further, the present invention provides an optical recording medium which is free from corrosion or pitting of the laminate film due to residual monomer, etc., in the resinous protective layer, is free from deterioration, has minimized warp or skew and thus can retain a long term reliability.

Hereinbelow, the present invention will be explained in more detail with reference to the Examples.

EXAMPLE 1

A 1.2 mm-thick polycarbonate substrate having a guide groove and a preformat pit was coated with a 500 Å-thick Si_3N_4 layer 2 by sputtering (pressure: 0.2 Pa, input power: 500 W), a laminate magnetic recording layer 3 including a 400 Å-thick amorphous GdTb layer and a 400 Å-thick TbFe layer respectively formed by sputtering (pressure: 0.3 Pa, input power: 500 W) and then with a 700 Å-thick Si_3N_4 layer formed by sputtering (pressure: 0.2 Pa, input power: 500 W) to form a laminate film 6 having a compression stress of about 30 kg/mm^2. Separately, an acrylate-type ultraviolet-curable resin having the following composition was provided.

(Composition)	
Caprolactone-modified dipentaerythritol hexaacrylate (trade name: KAYARAD DPCA-30, mfd. by Nihon Kayaku K.K.)	50 wt. %
Dioxane glycol diacrylate (trade name: KAYARAD R-604, mfd. by Nihon Kayaku K.K.)	45 wt. %
Photopolymerization initiator (trade name: IRG-184, mfd. by Ciba-Geigy A.G.)	5 wt. %

The ultraviolet-curable resin was applied on the laminate film by spin coating at 4000 rpm for 7 sec., followed by curing with irradiation from a UV lamp 7 issuing rays at a wavelength of 365 nm and an intensity on the surface of 233 mW/cm^2 for 7 sec., to form a 7 micron-thick resinous protective film having a tensile stress of 2–6 kg/mm^2, thereby obtaining an optical recording medium.

EXAMPLE 2

An optical recording medium was prepared in the same manner as in Example 1 except that the UV-curable resin was replaced by one having the following composition to form a protective resin layer having a tensile stress of 3.5 kg/mm^2.

(Composition)	
Caprolactone-modified dipentaerythritol hexaacrylate (KAYARAD DPCA-30, mfd. by Nihon Kayaku K.K.)	60 wt. %
Dioxane glycol diacrylate (KAYARAD R-604, mfd. by Nihon Kayaku K.K.)	35 wt. %
Photopolymerization initiator (IRG-184, mfd. by Ciba-Geigy A.G.)	5 wt. %

EXAMPLE 3

An optical recording medium was prepared in the same manner as in Example 1 except that the UV-curable resin was replaced by one having the following composition to form a protective resin layer having a tensile stress of 5.0 kg/mm^2.

(Composition)	
Caprolactone-modified dipentaerythritol hexaacrylate (KAYARAD DPCA-30, mfd. by Nihon Kayaku K.K.)	70 wt. %
Dioxane glycol diacrylate (KAYARAD R-604, mfd. by Nihon Kayaku K.K.)	25 wt. %
Photopolymerization initiator (IRG-184, mfd. by Ciba-Geigy A.G.)	5 wt. %

EXAMPLE 4

An optical modulation-type overwritable optical recording medium was prepared in the same manner as in Example 1 except that the laminate film was formed by sputtering on the polycarbonate substrate **1** so as to

comprise a 600 Å-thick SiN layer 2 (sputtering pressure: 0.3 Pa, input power: 500 W), a laminate magnetic layer 3 including a 400 Å-thick TbFeCo magnetic layer and an 800 Å-thick GdDyFeCo magnetic layer (sputtering pressure: 0.3 Pa, input power: 500 W) and a 900 Å-thick SiN layer (sputtering pressure: 0.3 Pa, input power: 500 W) to have a compression stress of 30 kg/mm^2.

COMPARATIVE EXAMPLE 1

An optical recording medium was prepared in the same manner as in Example 1 except that the UV-curable resin was replaced by one having the following composition to form a protective resin film having a tensile stress of 1.2 kg/mm^2.

(Composition)	
Neopentyl glycol diacrylate (di-functional) (KAYARAD-NPGDA, Nihon Kayaku K.K.)	40 wt. %
TMPA (tri-functional) (KAYARAD-TMPTA, Nihon Kayaku K.K.)	40 wt. %
Dicyclopentenyl acrylate (FA-57A, Hitachi Kasei K.K.)	10 wt. %
Photopolymerization initiator (KAYACURE BP, Nihon Kayaku K.K.)	10 wt. %

COMPARATIVE EXAMPLES 2 AND 3

Optical recording media were prepared in the same manner as in Example 1 except for using the following compositions for preparing the resinous protective layers.

(Composition for Comparative Example 2)	
Dipentaerythritol hexaacrylate (hexa-functional) (DPCA-60, mfd. by Nihon Kayaku K.K.)	50 wt. %
Dicyclopentenyl acrylate (mono-functional)	40 wt. %
Urethane acrylate (Allonix M-1100, mfd. by Toa Gosei Kagaku K.K.)	5 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.	5 wt. %

(Composition for Comparative Example 3)	
Dipentaerythritol hexaacrylate (hexa-functional) (DPCA-60, Nihon Kayaku K.K.)	40 wt. %
Urethane acrylate (Arronix M-1100, Toa Gosei Kagaku K.K.)	20 wt. %
TMPTA (KAYARAD-TMPTA, Nihon Kayaku K.K.)	35 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %

COMPARATIVE EXAMPLE 4

A 1.2 mm-thick polycarbonate substrate 1 having a guide groove and a preformat pit was coated with a 500 Å-thick inorganic dielectric layer of Si_3N_4 formed by sputtering (pressure: 0.4 Pa, input power: 500 W), a laminate opto-magnetic recording layer 3 including a 400 Å-thick amorphous GdTb layer and a 400 Å-thick amorphous TbFe layer respectively by sputtering (pressure: 0.6 Pa, input power: 550 W), and then with a 700 Å-thick inorganic dielectric layer of SiN formed by sputtering (pressure: 0.4 Pa, input power: 500 W) to form a laminate film having a compression strength of 11 kg/mm^2, followed by coating with a 7 micron-thick protective layer of a photo-cationically polymerizable epoxy resin (trade name: KR-400, mfd. by Asahi Denka K K.) to form an optical recording medium.

The optical recording medium was accompanied with little warp or skew and no increase in warp or skew was observed after a durability test, but the laminate film caused a crack to result in corrosion in the recording layer.

Tables 1 and 2 appearing at the end hereof summarize measured data of warp, skew, C/N value and B.E.R. for the optical recording media prepared in the above Examples and Comparative Examples as prepared and after a durability test for 2000 hours under the conditions of 80° C. and 90% RH, and the stress values in the resinous protective layers and laminate films in the media.

The measurement of C/N value and B.E.R. were performed by using an optomagnetic recording and reproduction tester (trade name: OS-2000, mfd. by Nakamichi K.K.) for recording and reproducing 5 MHz signals at a revolution speed of 1800 rpm and reproduction at a laser power of 5 mW.

EXAMPLE 5

An optical recording medium was prepared in the same manner as in Example 1 except that the UV-curable resin was replaced by one having the following composition to form a protective resin layer having a tensile stress of 4.9 kg/mm^2.

(Composition)	
Caprolactone-modified dipentaerythritol hexaacrylate (hexa-functional) (KAYARAD DPCA-30, mfd. by Nihon Kayaku K.K.)	85 wt. %
Urethane acrylate (Arronix M-1100, Toa Gosei Kagaku K.K.)	10 wt. %
Photopolymerization initiator (IRG-184, mfd. by Ciba-Geigy A.G.)	5 wt. %

EXAMPLES 6-9

Optical recording media were prepared in the same manner as in Example 1 except for using the following composition for preparing the resinous protective layers.

(Composition for Example 6)	
Dipentaerythritol monohydroxypentaacrylate (penta-functional) (SR-399, mfd. by Sartomer Co.)	90 wt. %
Urethane acrylate (Allonix M-1100, mfd. by Toa Gosei Kagaku K.K.)	5 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %

(Composition for Example 7)	
Alkyl-modified dipentaerythritol pentaacrylate (penta-functional) (KAYARAD D-310, Nihon Kayaku K.K.)	94 wt. %
Urethane acrylate (ARTRESIN UN-9000, Negami Kogyo K.K.)	4 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	2 wt. %

(Composition for Example 8)	
Alkyl-modified dipentaerythritol pentaacrylate (penta-functional) (KAYARAD D-310, Nihon Kayaku K.K.)	62 wt. %
Urethane acrylate (ARTRESIN UN-9000, Negami	4 wt. %

-continued

(Composition for Example 8)	
Kogyo K.K.)	
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %
TMPTA (KAYARAD-TMPTA, Nihon Kayaku K.K.)	15 wt. %
MANDA (KAYARAD-MANDA, Nihon Kayaku K.K.)	14 wt. %

(Composition for Example 9)	
Dipentaerythritol monohydroxypentaacrylate (SR-399)	75 wt. %
Urethane acrylate (ARTRESIN UN-9000, Negami Kogyo K.K.)	6 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %
MANDA (KAYARAD-MANDA, Nihon Kayaku K.K.)	14 wt. %

(Composition for Example 10)	
Dipentaerythritol hexaacrylate (hexa-functional) (KAYARAD DPCA-30, Nihon Kayaku K.K.)	90 wt. %
TMPTA (tri-functional) (KAYARAD TMPTA, Nihon Kayaku K.K.)	5 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %

(Composition for Example 11)	
Dipentaerythritol hexaacrylate (hexa-functional) (KAYARAD DPCA-30, Nihon Kayaku K.K.)	85 wt. %
Bisphenol A diglycidyl ether (Epikote 828, Yuka Shell K.K.)	10 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %

EXAMPLE 12

A 1.2 mm-thick polycarbonate substrate **1** having a guide groove and a preformat pit was coated with a 100 Å-thick inorganic dielectric layer of SiN formed by sputtering (pressure: 0.25 Pa, input power: 500 W), a laminate recording layer **3** including a 100 Å-thick amorphous GdFeCo layer and a 200 Å-thick amorphous TbFeCo layer respectively by sputtering (pressure: 0.4 Pa, input power: 540 W), and then with a 300 Å-thick inorganic dielectric layer **4** of SiN formed by sputtering (pressure: 0.25 Pa, input power: 500 W) to form a laminate film having a compression strength of 15 kg/mm^2.

Then, a UV-curable resin having a composition shown below was applied by spin coating (4000 rpm, 7 sec) on the laminate film and then cured by irradiation from a UV lamp **6** issuing UV rays of 365 nm having a intensity on the surface of 233 mW/cm^2 for 7 sec., to form a 7 micron-thick resinous protective layer **5**, thereby obtaining an optical recording medium.

(Composition)	
Alkyl-modified dipentaerythritol pentaacrylate (penta-functional) (KAYARAD D-310, Nihon Kayaku K.K.)	62 wt. %
Urethane acrylate (Allonix M-1100, Toa Gosei Kagaku K.K.)	4 wt. %
Photopolymerization initiator (IRG-184, Nihon Ciba-Geigy K.K.)	5 wt. %
TMPTA (KAYARAD-TMPTA, Nihon Kayaku K.K.)	15 wt. %
MANDA (KAYARAD-MANDA, Nihon Kayaku K.K.)	14 wt. %

The measured data of warp, skew, C/N value and B.E.R. for the optical recording media according to the above Examples 5–12 as prepared and after a durability test for 2000 hours under the conditions of 80° C. and 90 % RH, and the stress values in the resinous protective layers and the laminate films, are also shown in Tables 1 and 2 appearing at the end.

As shown in Table 1, the optical recording media obtained in Example 1 showed improvements in respects of warp and skew even in the initial stage and showed substantially no increase in warp or skew even after the durability test.

Further, as shown in Examples 5–9 and 12, when a photocurable composition comprising 60 wt. % or more of a polyfunctional acrylate compound having 5 or more functional groups and 10 wt. % or less of a urethane acrylate was used for constituting the resinous protective layer, there was provided an optical recording medium which caused no corrosion in the laminate film, no decrease in C/N value or no increase in B.E.R.

On the other hand, as shown in Table 2, Comparative Examples 1, 2 and 3 provided optical recording media which showed warp and skew which were large even at the initial stage and further increased after the durability test, due to a small stress in the resinous protective layer. Further, these media caused corrosion or pitting in the optical recording, thus causing a deterioration in both C/N value and B.E.R. Further, the medium according to Comparative Example 4 having a small stress in the laminate film caused a decrease in warp and skew but also resulted in a crack in the laminate film.

The stress referred to herein in the resinous protective layers is based on values measured according to the following method. Referring to FIG. 3, a silicon disk substrate **10** is coated with a sample photocurable resin composition used for constituting the resinous protective layer, followed by curing, to form a prescribed thickness (5–8 microns) of a cured film **9**. The coated substrate is placed on a stress gauge **11** (mfd. by Ionic Systems K.K.), the resultant warp d is measured as shown in FIG. 3, and the stress σ in the cured resin film is calculated according to the following equation (1).

$$\sigma=(d/r^2)\,[Es/3(1-\nu)]\,(Ts^2/Tf) \tag{1}$$

wherein
- Es: Young's modulus of the silicon substrate,
- ν: Poisson ratio of the silicon substrate,
- Ts: thickness of the silicon substrate,
- Tf: thickness of the cured resin film, and
- r: radius of the silicon substrate.

Further, the stress in the laminate film is based on values measured according to the following method. That is, the stress σ' in the laminate film **6** is calculated according to the following equation (2).

$$\sigma'=Eb^2/6(1-\nu)rd \tag{2}$$

wherein
- E: Young's modulus of the substrate (constant),
- ν: Poisson ratio of the substrate (constant),

r: radius of curvature resultant in the substrate, having the laminate film 6 thereon,

"After test" in the heading means the value after the durability test.

TABLE 1

	Warp l (μm)		Skew (°)		Stress (kg/mm²)		C/N (dB)			B.E.R.		
	Initial	After test	Initial	After test	Resin layer	Laminate film	Initial	After test	Evaluation	Initial	After test	Evaluation
Ex.												
1	−18	−19	0.11	0.12	+2.6	−30	51	45	B	1.0×10^{-6}	0.8×10^{-4}	B
2	−20	−20	0.13	0.13	+3.5	−27	50	44	B	1.0×10^{-6}	1.0×10^{-4}	B
3	−22	−22	0.14	0.14	+5.0	−33	50	45	B	1.0×10^{-6}	1.0×10^{-4}	B
4	−16	−17	0.10	0.10	+2.8	−30	51	44	C	1.0×10^{-6}	1.1×10^{-4}	B
5	−10	−12	0.08	0.09	+4.9	−30	50	49	A	1.0×10^{-6}	0.9×10^{-6}	A
6	−8	−9	0.07	0.07	+5.0	−27	52	51	A	1.0×10^{-6}	1.0×10^{-6}	A
7	−5	−7	0.05	0.06	+5.3	−33	53	50	A	0.8×10^{-6}	0.9×10^{-6}	A
8	−18	−18	0.13	0.13	+3.7	−30	52	50	A	1.1×10^{-6}	1.0×10^{-6}	A
9	−13	−14	0.11	0.10	+4.2	−32	53	52	A	1.0×10^{-6}	0.9×10^{-6}	A
10	−20	−19	0.10	0.12	+5.2	−31	50	40	C	1.0×10^{-6}	1.1×10^{-2}	D
11	−10	−11	0.09	0.10	+4.8	−29	51	43	C	1.0×10^{-6}	0.7×10^{-3}	C
12	−7	−9	0.06	0.07	+3.7	−15	53	52	A	0.8×10^{-6}	0.9×10^{-6}	A

TABLE 2

	Warp l (μm)		Skew (°)		Stress (kg/mm²)		C/N (dB)			B.E.R.		
	Initial	After test	Initial	After test	Resin layer	Laminate film	Initial	After test	Evaluation	Initial	After test	Evaluation
Comp. Ex.												
1	−130	−179	0.32	0.39	+1.2	−29	50	41	C	0.4×10^{-6}	1.0×10^{-3}	C
2	−25	−27	0.21	0.23	+2.3	−28	52	42	C	1.1×10^{-6}	1.0×10^{-3}	C
3	−139	−180	0.35	0.37	+1.9	−30	49	39	C	1.0×10^{-6}	1.0×10^{-3}	C

d: thickness of the laminate film, and

b: thickness of the substrate (constant).

Herein, referring to FIG. 4, the radius of curvature r is calculated by measuring the number of Newton rings m resultant on the laminate film 6 formed on the substrate 1 by means of a Zygo's interferometer 41 including a light source 12, lenses 13, a filter 14 and a camera 15, and by using the following equation (3).

$$r = a^2/m\lambda \qquad (3)$$

wherein

a: radius of the substrate, and

λ: wavelength of light from the source 12 in the interferometer.

The warp and skew are based on values measured by a flatness tester (trade name: KS-916, mfd. by Anritsu Denki K.K.).

The measured data for the above Examples and Comparative Examples are summarized in the following Tables 1 and 2, wherein the evaluation was performed according to the following standards:

[C/N]

The decrease in C/N value after the durability test was classified according to the following standards:

A: 3 dB or below, B: 4–5 dB, C: 7 dB or above.

[B.E.R.]

The value after the durability test was classified according to the following standards:

A: Retained at a level of 10^{-6}

B: Lowered to a level of 10^{-4}

C: Lowered to a level of 10^{-3}

D: Lowered to a level of 10^{-2}

Further, the sign "−" before the value of warp indicates that the warp occurred to form a convexity on the laminate film side.

The sign "+" before the stress value indicates a tensile stress and the sign "−" indicates a compression stress.

What is claimed is:

1. An optical recording medium comprising: a resinous substrate, a laminate film including an inorganic dielectric layer and a recording layer, and a resinous protective film, disposed on the substrate; wherein the resinous protective layer has a tensile stress of 2.5–5.5 kg/mm², and the laminate film has a compression stress of 15–55 kg/mm².

2. A medium according to claim 1, wherein the resinous protective film comprises a cured film of a photocurable resin.

3. A medium according to claim 1, wherein the recording layer comprises an inorganic compound.

4. A medium according to claim 1, wherein the inorganic dielectric layer is disposed on both sides of the recording layer to form the laminate film.

5. A medium according to claim 3, wherein the recording layer has a laminated structure including a plurality of layers comprising mutually different inorganic compounds.

6. A medium according to claim 1, wherein the inorganic dielectric layer comprises at least one species selected from the group consisting of Si_3N_4, SiO_x, ZnS and SiC.

7. A medium according to claim 1, wherein the recording layer has a thickness of 200–1000 Å.

8. A medium according to claim 1, wherein the inorganic dielectric layer has a thickness of 400–1000 Å.

9. A medium according to claim 2, wherein the photo-curable resin comprises 60 wt. % or more of a polyfunctional acrylate compound having 5 or more functional groups and 10 wt. % or less of a urethane acrylate compound.

10. A medium according to claim 9, wherein the polyfunctional acrylate compound comprises dipentaerythritol hexaacrylate.

11. A medium according to claim 9, wherein the urethane acrylate compound is contained in a proportion of 2-8 wt. % of the photo-curable resin.

12. A medium according to claim 1, wherein the recording layer comprises an amorphous magnetic recording layer.

13. A medium according to claim 1, wherein the laminate film includes a reflecting layer.

14. A medium according to claim 1, wherein the resinous protective layer has a tensile stress of 3-5 kg/mm^2.

15. A medium according to claim 1, wherein the laminate film has a compression stress of 20-50 kg/mm^2.

16. An optical recording medium, comprising: a resinous substrate, a laminate film including an inorganic dielectric layer and a recording layer, and a resinous protective film, disposed on the substrate; wherein the resinous protective layer comprises a cured film of a photocurable resin comprising 60 wt. % or more of a polyfunctional acrylate compound having 5 or more functional groups and 10 wt. % or less of a urethane acrylate compound.

17. A medium according to claim 16, wherein the polyfunctional acrylate compound comprises dipentaerythritol hexaacrylate.

18. A medium according to claim 16, wherein the urethane acrylate compound is contained in a proportion of 2-8 wt. % of the photo-curable resin.

19. A process for producing an optical recording medium, comprising:

coating resinous substrate with a laminate film including an inorganic dielectric layer and a recording layer so as to provide the laminate film with a compression stress of 15-55 kg/mm^2, and

coating the laminate film with a resinous protective layer so as to provide the resinous protective layer with a tensile stress of 2.5-5.5 kg/mm^2.

20. A process according to claim 19, wherein the laminate film is formed by sputtering or evaporation.

21. A process according to claim 19, wherein the laminate film is formed to have a compression stress of 20-50 kg/mm^2, and the resinous protective film is formed to have a tensile stress of 3-5 kg/mm^2.

22. A process according to claim 19, wherein the laminate film is formed by sputtering.

* * * * *

Appendix D

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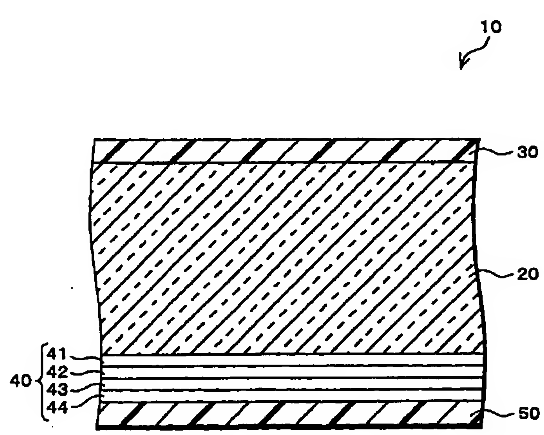
(54) Optical information recording medium

(57) An optical information recording medium includes a transparent substrate, a thin film layer formed on said transparent substrate and having a recording film, a thin film protecting film formed on said thin film layer, and a substrate protecting film formed on said transparent substrate. A neutral plane of deformation caused by a temperature change of the optical information recording medium is present within the thin film layer. Consequently, it has become possible to provide an optical information recording medium which can prevent deformation (warpage) caused by temperature and humidity changes and be readily manufactured.

FIG. 1



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Description

FIELD OF THE INVENTION

[0001] The present invention relates to an optical information recording medium for recording and reproducing information, and more particularly, to an optical information recording medium which can suppress warpage caused by a change in environments or variance with time.

BACKGROUND OF THE INVENTION

[0002] As an example optical information recording medium for recording and reproducing information, a thin disk type has been known. Figure 6(a) is a plan view of such an optical information recording medium and Figure 6(b) is a side elevation thereof.

[0003] Figure 7 is a schematic cross section showing an arrangement of a conventional optical information recording medium 110.

[0004] As shown in Figure 7, the conventional optical information recording medium 110 includes a disk (see Figure 6(a)) substrate 120 made of polycarbonate or the like, on which a single- or multi-layer thin film layer 140 comprising thin films, such as dielectric films 141 and 143 (silicon nitride, etc.), a recording film 142 (TbFeCo, etc.), and a reflecting film 144 (Al, etc.), is formed by means of sputtering or the like.

[0005] Also, a thin film protecting film 150 made of a resin film or the like is formed on the thin film layer 140, and a substrate protecting film 130 made of resin or the like is formed on the light incident surface of the substrate 120.

[0006] The thicknesses of these films and layers are as follows: the thickness of the substrate 120 is approximately 1.2 mm; the thickness of the single- or multi-layer thin film layer 140 formed by means of sputtering or the like is 10-30 nm; the thickness of the thin film protecting film 150 is 1-30 μm; and the thickness of the substrate protecting film 130 is 1-30 μm. Thus, the substrate 120 made of polycarbonate occupies most of the optical information recording medium 110 in thickness.

[0007] The rigidity of the optical information recording medium 110 depends almost entirely on the substrate 120, and because the substrate 120 is sufficiently thick, deformation caused by a change in environments (temperature and humidity changes) is quite small. For this reason, a balance of stress and a bending moment of each layer has not been considered generally in most of the cases.

[0008] However, there has been a demand to further increase recording and reproducing density of the optical information recording medium, and the substrate has been made thinner (for example, the thickness is now reduced to 0.6 mm from 1.2 mm) to suppress the occurrence of aberration. As a result, the rigidity of the optical information recording medium is reduced, and larger deformation occurs due to stress produced in each layer forming the optical information recording medium with a change in environments (temperature and humidity changes), thereby posing a problem that information can not be readily recorded and reproduced. Thus, there has been an increasing need for an optical information recording medium which can maintain good performance in response to a change in environments even if its rigidity is reduced by employing a thinner substrate.

[0009] Japanese Laid-open Patent Application No. 195745/1992 (Japanese Official Gazette, *Tokukaihei No. 4-195745*, published on July 15, 1992) discloses a technique of suppressing deformation of the optical information recording medium, by which a warpage preventing dielectric film is provided on the back surface (the surface on which the thin film layer is not formed) of the substrate (prior art ①).

[0010] Figure 8 is a cross section showing an arrangement of the above optical information recording medium (prior art ①). In Figure 8, like components are labeled with like reference numerals with respect to Figure 7 for ease of explanation. As shown in Figure 8, a dielectric layer 160 is provided on the light incident side of the substrate 120 made of polycarbonate, so that the same expansion coefficient is given to the recording film 142 and dielectric layer 160 which are provided respectively at the both sides of the transparent substrate 120. Consequently, because the optical information recording medium has a symmetrical structure with respect to the substrate 120, warpage of the optical information recording medium can be prevented.

[0011] Also, Japanese Laid-open Patent Application No. 64119/1998 (Japanese Official Gazette, *Tokukaihei No. 10-64119*, published on March 6, 1998) discloses that, by making a thin film protecting film thicker (30-50 μm), warpage occurring with increasing temperatures can be prevented (prior art ②).

[0012] Further, Japanese Laid-open Patent Application No. 364248/1992 (Japanese Official Gazette, *Tokukaihei No. 4-364248*, published on December 16, 1992) proposes an optical information recording medium which can solve problematic warpage caused by a humidity change. This optical information recording medium includes, as shown in Figure 9, a thin film protecting film 150, a thin film layer 140, a substrate 120, a substrate protecting film 130, and in order to solve the problem, it additionally includes a moisture permeation preventing film 170 made of SiO_2, AlN, etc. between the substrate 120 and substrate protecting film 130 (prior art ③). In Figure 9, like components are labeled with

like reference numerals with respect to Figures 7 and 8 for ease of explanation.

[0013] However, according to the technique disclosed in Japanese Laid-open Patent Application No. 195745/1992 *supra* (see Figure 8, prior art ①), the dielectric layer 160 has to be provided on the light incident side of the substrate 120 by means of sputtering or the like. In this case, the manufacturing procedure includes forming the thin film layer 140 on one surface of the substrate 120, turning over the substrate 120, and forming the dielectric layer 160 on the opposite surface. Thus, not only the manufacturing procedure becomes complex, but also expensive manufacturing facility is required, thereby posing a problem that the manufacturing costs are undesirably increased.

[0014] Also, the technique (prior art ②) of Japanese Laid-open Patent Application No. 64119/1998 *supra* poses a problem that the thin film protecting film is so thick that it can not be readily formed. In addition, in case that the optical information recording medium is a magneto-optical recording medium, for example, in order to turn an applied magnetic field inversely at a high speed while information is being recorded, it is preferable to approximate the thin film layer to magnetic field generating means. However, a too thick thin film protecting film can cause problematic deterioration of magnetic characteristics.

[0015] Further, the technique of Japanese Laid-open Patent Application No. 364248/1992 *supra* (see Figure 9, prior art ③) demands the moisture permeation preventing film 170 made of SiO_2, AlN, etc. to be provided on the light incident side of the substrate 120 by means of sputtering or the like. In this case, the manufacturing procedure includes forming the thin film layer 140 on one surface of the substrate 120, turning over the substrate 120, and forming the moisture permeation preventing film 170 on the opposite surface. Thus, not only the manufacturing procedure becomes complex, but also expensive manufacturing facility is required, thereby posing a problem that the manufacturing costs are undesirably increased.

SUMMARY OF THE INVENTION

[0016] It is therefore an object of the present invention to provide an optical information recording medium which can prevent deformation (warpage) caused by temperature and humidity changes and be readily manufactured.

[0017] In order to fulfill the above and other objects, an optical information recording medium of the present invention is characterized by being furnished with:

a thin film layer, formed on a substrate, for recording and reproducing information; and
a thin film protecting film, formed on the thin film layer, for protecting the thin film layer,
a neutral plane of deformation in a thickness direction caused by a temperature change being present in a vicinity of the thin film layer.

[0018] According to the above arrangement, the optical information recording medium has a multi-layer structure in which the thin film layer and thin film protecting film are formed on the substrate.

[0019] If the substrate is made thinner in the optical information recording medium having such a multi-layer structure, the rigidity is reduced, thereby posing a problem that warpage occurs in the thickness direction toward the thin film protecting film in response to a temperature change.

[0020] To solve the above problem, a conventional optical information recording medium employing a thin substrate is additionally provided with a warpage preventing dielectric layer. This solution, however, raises another problem that, by providing the additional layer, the number of manufacturing steps and manufacturing costs are undesirably increased. In particular, because the dielectric layer is formed on the opposite side (the side opposite to the side where the thin film layer is formed) of the substrate, the substrate has to be turned over after the thin film layer is formed. Accordingly, not only the manufacturing procedure becomes complex, but also expensive manufacturing facility is required, thereby increasing the manufacturing costs.

[0021] In contrast, according to the arrangement of the present invention, the neutral plane of deformation in the thickness direction caused by a temperature change is present in the vicinity of the thin film layer. In other words, bending moments applied on the thin film layer from the substrate side and thin film protecting film side are substantially cancelled out with each other.

[0022] More specifically, warpage of the optical information recording medium in the direction toward the thin film protecting film is caused by a bending moment applied on the thin film layer from the substrate side. Thus, according to the arrangement of the present invention, the bending moment applied on the thin film layer from the substrate side is cancelled out with a bending moment applied thereon from the thin film protecting film side, and the vicinity of the thin film layer serves as the neutral plane of deformation in the thickness direction. Hence, the optical information recording medium of the present invention causes warpage neither in the thickness direction nor in the opposite direction.

[0023] Consequently, different from the conventional arrangement, the additional warpage preventing dielectric layer can be omitted, thereby eliminating the problem that the manufacturing procedure becomes complex and the manufacturing costs are increased.

[0024] In order to fulfill the above and other objects, another optical information recording medium of the present invention is characterized by being furnished with:

a thin film layer, formed on a substrate, for recording and reproducing information;
a thin film protecting film, formed on the thin film layer, for protecting the thin film layer; and
a substrate protecting film, formed on the substrate on a surface opposite to a surface where the thin film layer is formed, for protecting the substrate,
a moisture permeation degree of the substrate protecting film being smaller than a moisture permeation degree of the thin film protecting film.

[0025] In case of the optical information recording medium in which the thin film layer and thin film layer protecting film are formed on one side of the substrate and the substrate protecting film on the other side, only a slight quantity of water is absorbed from the external and reaches the substrate in the thin film protecting film side because of the thin film layer interposed therebetween, whereas water readily reaches the substrate in the substrate protecting film side. Thus, there is a problem that a volume change occurs locally on the substrate in response to a humidity change, thereby causing warpage of the optical information recording medium.

[0026] In order to solve such a problem, a conventional optical information recording medium is additionally provided with a moisture permeation preventing film which can prevent warpage caused by a humidity change. This solution, however, raises another problem that, by providing the additional layer, the number of manufacturing steps and manufacturing costs are undesirably increased. In particular, because the moisture permeation preventing film is provided between the substrate and substrate protecting film, the substrate has to be turned over after the thin film layer is formed. Accordingly, not only the manufacturing procedure becomes complex, but also expensive manufacturing facility is required, thereby increasing the manufacturing costs.

[0027] In contrast, according to the arrangement of the present invention, a moisture permeation degree of the substrate protecting film is smaller than that of the thin film protecting film. Hence, because absorption of water from the substrate protecting film side can be reduced, warpage of the optical information recording medium caused by a humidity change can be suppressed.

[0028] Consequently, different from the conventional arrangement, the additional moisture permeation preventing film can be omitted, thereby eliminating the problem that the manufacturing procedure becomes complex and the manufacturing costs are increased.

[0029] For a fuller understanding of the nature and advantages of the invention, reference should be made to the ensuing detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030]

Figure 1 is a schematic cross section showing an arrangement of an optical information recording medium in accordance with an embodiment of the present invention;
Figures 2(a) and 2(b) are views explaining warpage of the optical information recording medium;
Figure 3 is a view explaining a multi-layer beam;
Figure 4 is a view showing time dependency of a variation of warpage angles in response to a temperature change;
Figure 5 is a view showing time dependency of a variation of warpage angles in response to a humidity change;
Figure 6(a) is a plan view showing an arrangement of a typical optical information recording medium, and Figure 6(b) is a side elevation thereof;
Figure 7 is a schematic cross section showing an arrangement of a conventional optical information recording medium;
Figure 8 is a schematic cross section showing an example of a conventional optical information recording medium;
Figure 9 is a schematic cross section showing another example of a conventional optical information recording medium;
Figure 10 is a view showing time dependency of a variation of warpage angles in response to a temperature change in an optical information recording medium as one example of the present invention; and
Figure 11 is a view showing time dependency of a variation of warpage angles in response to a humidity change in an optical information recording medium as one example of the present invention.

DESCRIPTION OF THE EMBODIMENTS

(Embodiment 1)

[0031] The following will explain an optical information recording medium of the present embodiment, and the principle of the present invention will be given in the first place.

① Principle

[0032] As has been discussed in the BACKGROUND OF THE INVENTION, the optical information recording medium disclosed in Japanese Laid-open Patent Application No. 195745/1992 *supra* (see Figure 8) suppresses warpage of the optical information recording medium by forming the layers symmetrically with respect to the transparent substrate 120.

[0033] In this regard, with an optical information recording medium 10 including, as shown in the schematic cross section of Figure 1, a thin film protecting film 50, a thin film layer 40, a transparent substrate (substrate) 20, and a substrate protecting film 30, the inventors of the present invention discovered that (a) warpage of the optical information recording medium 10 can be suppressed by positioning the thin film layer 40 (or the vicinity thereof) at the center of deformation caused by a temperature change, that is, making the optical information recording medium 10 symmetrical with respect to the thin film layer 40, and (b) the thin film protecting film 50 can be made thinner while warpage is suppressed. This will be described more in detail in the following.

[0034] As shown in Figure 1, the optical information recording medium 10 includes the transparent substrate 20 made of polycarbonate or the like, on which the single-or multi-layer thin film layer 40 comprising thin films, such as dielectric films 41 and 43 (silicon nitride, etc.), a recording film 42 (TbFeCo, etc.), and a reflecting film 44 (Al, etc.), is formed by means of sputtering or the like. In addition, the thin film protecting film 50 mainly made of resin is formed on the thin film layer 40, and the substrate protecting film 30 mainly made of resin is formed on the transparent substrate 20 on the opposite surface to the surface where the thin film layer 40 is formed, so that the transparent substrate 20 is protected.

[0035] As has been discussed, the optical information recording medium is generally composed of multiple layers, and because each layer has different linear expansion coefficient as one of the physical properties, stress produced in each layer in response to a temperature change is also different.

[0036] To be more specific, the transparent substrate 20 made of polycarbonate, substrate protecting film 30, and thin film protecting film 50 normally have larger linear expansion coefficients than the thin film layer 40, and expansion of the thin film layer 40 in the radius direction of the substrate is quite small compared with that of the other layers. Also, the thickness of the transparent substrate 20 is quite large compared with the thicknesses of the substrate protecting film 30 and thin film protecting film 50, and each thin film forming the thin film layer 40 has quite large Young's modulus compared with the other layers. Thus, in response to a temperature change, the thin film layer 40 expands slightly while the transparent substrate 20 expands significantly. As a result, the optical information recording medium 10 readily causes warpage in a direction perpendicular to the radius direction toward the thin film protecting film 50 in the film thickness direction. Figure 2(a) is a plan view schematically explaining warpage, and Figure 2(b) is a side elevation thereof.

[0037] In the present embodiment, in order to prevent such warpage, a bending moment is applied to the thin film layer 40 in the opposite direction to a bending moment applied thereto from the transparent substrate 20 by adjusting the linear expansion coefficient, Young's modulus, and film thickness of the thin film protecting film 50 formed on the thin film layer 40. Then, by using a plane parallel to the film surface within the thin film layer 40 (or in the vicinity thereof) as a neutral plane of deformation, deformation (warpage shown in Figures 2(a) and 2(b)) caused by a temperature change can be suppressed.

[0038] To be more specific, the optical information recording medium 10 of the present invention is arranged in such a manner that a neutral plane of deformation in the thickness direction caused by a temperature change is present in the vicinity of the thin film layer 40. In other words, the optical information recording medium 10 of the present invention is arranged in such a manner that bending moments applied on the thin film layer 40 from the substrate 20 side and thin film protecting film 50 side in response to a temperature change are substantially cancelled out with each other.

[0039] In order to realize such an arrangement, the thickness, Young's modulus, linear expansion coefficient of each of the substrate 20, thin film layer 40, and the thin film protecting film 50 (particularly the thin film protecting film 50) are set to their respective desired values.

[0040] The linear expansion coefficient, Young's modulus, film thickness of the thin film protecting film 50 are set in accordance with the approximate calculations set forth below.

[0041] In the optical information recording medium 10, three kinds of stress are produced in response to a temperature change: stress (axial tension) applied in the radius direction; stress applied in a circumferential direction; and

stress applied in the film thickness direction. However, because the optical information recording medium 10 is a disk, the stress applied in the circumferential direction is even within the circumference, and a force in the film thickness direction is applied evenly within each layer. Therefore, these two kinds of stress can be assumed as non-contributing factors to deformation. Hence, deformation, that is, warpage (see Figures 2(a) and 2 (b)), of the optical information recording medium 10 can be replaced with warpage in a multi-layer beam which corresponds to the cross section of the same. Figure 3 shows the multi-layer beam, in which n-layer beam are illustrated, where n represents the number of layers in the optical information recording medium. In case of the optical information recording medium 10 of Figure 1, n=7.

[0042] Warpage angles θ in the multi-layer beam in response to a temperature change can be expressed by following Equations (1) through (5) derived from a balance of the axial tension P_i (i=1, 2, ..., n) and bending moment M_i in each layer:

$$M_i = E_i I_i / R_i \tag{1}$$

$$\alpha_i T + (P_i / bt_i E_i) - (t_i / 2R_i) = \alpha_{i+1} T + (P_{i+1} / bt_{i+1} E_{i+1}) + (t_{i+1} / 2R_{i+1}) \tag{2}$$

$$\sum_{i=1}^{n} P_i = 0 \tag{3}$$

$$\sum_{i=1}^{n} M_i + P_1\{y-(t_1/2)\} + P_2\{y-t_1-(t_2/2)\} + \cdots + P_n\{y-t_1-t_2-\cdots-(t_n/2)\} = 0 \tag{4}$$

$$\theta = \tan^{-1}((L-2)/R \tag{5}$$

where

α_i:	linear expansion coefficient of the i layer
E_i:	Young's modulus of the i layer
t_i:	thickness of the i layer
P_i:	axial tension in the i layer
M_i:	bending moment in the i layer
R_i:	radius of curvature
I_i:	secondary moment of the i layer's cross section
b:	width of multi-layer beam (unit length)
T:	temperature change
L:	length of a beam
y:	neutral plane's position in the n-layer beam
θ:	warpage angles (see Figure 3) at the largest variation part when a length l=4 mm.

[0043] Because the thickness of each layer is far smaller than the radius of curvature, the radius of curvature (R_i) in each layer (i=1, 2, • • •, n) can be deemed as equal ($R_1=R_2=R_3=\cdots=R$). Also, a temperature change (T) is a temperature change in the usable temperature environment (generally, from -15°C to 80°C) of the optical information recording medium.

[0044] In Equations (1) through (5) above, the thickness, linear expansion coefficient (a), and Young's modulus (E) of each layer (particularly those of the thin film protecting film 50, because those of the thin film layer 40 are often determined in advance by characteristics of the optical information recording medium) are determined in such a manner that, when y is set within the thin film layer 40, small θ is given, that is, a large radius of curvature (R) is given. Consequently, an optical information recording medium which can suppress warpage shown in Figures 2(a) and 2(b) caused by a temperature change can be obtained.

[0045] Incidentally, when the thin film protecting film 50 in the optical information recording medium becomes thicker, it becomes more difficult to form the same by means of spin coating. Also, in case that the optical information recording medium is a magneto-optical recording medium, if the thin film protecting film 50 becomes thicker, the magnetic head is spaced apart farther from the thin film layer 40, which is not preferable from the view points of magnetic characteristics. In view of the foregoing, the film thickness of the thin film protecting film 50 is preferably set to 30 μm or less, and more preferably to 20 μm or less. Thus, the thin film protecting film 50 has to satisfy the above film thickness

condition (30 μm or less (preferably 20 μm or less)), and at the same time it has to be made of materials having the linear expansion coefficient (α) and Young's modulus (E) such that can reduce θ in Equations (1) through (5) above. According to Equations (1) through (5) above, even if the film thickness is small, θ can be reduced by making at least one of the linear expansion coefficient (α) and Young's modulus (E) large.

[0046] As has been discussed, with the optical information recording medium 10 of the present embodiment, the occurrence of warpage can be suppressed by setting the physical properties of each layer (particularly the thin film protecting film 50) in such a manner that the neutral plane of deformation caused by a temperature change is positioned within (or in the vicinity of) the thin film layer 40. In addition, of all the layers forming the optical information recording medium 10, the thin film layer 40 having the slowest deformation rate causes the slightest deformation, and overshoot of variation, which causes a problem when a temperature actually changes, also becomes small. Further, because only the substrate protecting film 30 mainly made of resin has to be formed on the light incident side of the transparent substrate 20, the optical information recording medium 10 can be manufactured more readily in comparison with the spin coating or the like, thereby simplifying the manufacturing procedure.

[0047] The above description explained that the physical properties of each of the layers (particularly the thin film protecting film 50) forming the optical information recording medium 10 are set by using the materials characteristics of these layers, so that the neutral plane of deformation caused by a temperature change is present within (or in the vicinity of) the thin film layer 40. However, in general, each layer forming the thin film layer 40 of the optical information recording medium 10 is so thin that the thin film layer 40 can be deemed as a single layer, and the physical properties of each layer (particularly the thin film protecting film 50) may be set in such a manner that the bending moments applied on the thin film layer 40 in response to a temperature change from the both sides (the transparent substrate 20 and substrate protecting film 30 side and the thin film protecting film 50 side) are substantially cancelled out with each other. In this case, warpage of the thin film layer 40 caused by a temperature change can be also eliminated almost completely. By taking the fact that the transparent substrate 20 has a considerable thickness into consideration, in order to reduce the thickness of the thin film protecting film 50 (30 μm or less (preferably 20 μm or less)), at least one of the linear expansion coefficient (α) and Young's modulus (E) of the thin film protecting film 50 has to be larger than those of the transparent substrate 20.

② Examples 1 and 2 and Comparative Example 1

[0048] Next, the following will explain examples of the optical information recording medium 10 formed based on the above principle. In Examples 1 and 2 and Comparative Example 1, the thin film layer 40 was made of an aluminum nitride layer alone. This is because, in most of the cases, deformation of the thin film layer 40 is caused by the dielectric layer made of aluminum nitride, etc. Also, in Examples 1 and 2 and Comparative Example 1, the substrate protecting film 30 was omitted. Thus, it should be appreciated that when the substrate protecting film 30 is formed, the physical properties of each layer (particularly the thin film protecting film 50) have to be set in consideration of the presence of the substrate protecting film 30.

[0049] A medium formed as Example 1 included a substrate (transparent substrate) 20 made of polycarbonate, on which an aluminum nitride thin film layer (thin film layer 40), and UV curable resin 1 (thin film protecting film 50) designed under the conditions in accordance with Equations (1) through (5) above were formed. An optical information recording medium formed as Comparative Example 1 included a polycarbonate substrate, on which an aluminum nitride thin film layer and convectional UV curable resin 2 (thin film protecting film) were formed. The arrangements of Example 1 and Comparative Example 1 are set forth in Table 1 and Table 2 below.

Table 1

Example 1				
	MATERIAL	FILM THICKNESS	YOUNG'S MODULUS (Pa)	LINEAR EXPANSION COEFFICIENT (1/°C)
TRANSPARENT SUBSTRATE	POLYCARBONATE	0.6 mm	2.41E+09	6.00E-05
THIN FILM LAYER	ALUMINUM NITRIDE	79 nm	3.43E+11	5.60E-06
THIN FILM PROTECTING FILM	UV CURABLE RESIN 1	16 μm	1.80E+09	7.10E-05

Table 2

Comparative Example 1				
	MATERIAL	FILM THICKNESS	YOUNG'S MODULUS (Pa)	LINEAR EXPANSION COEFFICIENT (1/°C)
TRANSPARENT SUBSTRATE	POLYCARBONATE	0.6 mm	2.41E+09	6.00E-05
THIN FILM LAYER	ALUMINUM NITRIDE	79 nm	3.43E+11	5.60E-06
THIN FILM PROTECTING FILM	UV CURABLE RESIN 2	15 μm	1.80E+09	5.62E-05

[0050] Table 1 and Table 2 reveal that the difference between Example 1 and Comparative Example 1 was the liner expansion coefficient of the UV curable resin (thin film protecting film 50), and the one having a larger linear expansion coefficient was used in Example 1. As the transparent substrate 20, a disk having the minor diameter of 15 mm and the major diameter of 120 mm was used in both Example 1 and Comparative Example 1.

[0051] A temperature change (T=30°C) was given to the media of Example 1 and Comparative Example 1 (temperatures of the media were raised from 25°C to 55°C), and a variation of warpage angles θ at the outer circumference portion (r=56 mm) with time was analyzed. The reason why a variation of warpage angles was analyzed instead of the warpage angles itself is because the medium has its own warpage angles at normal temperature, and the warpage angles itself does not precisely represent deformation caused by a temperature change.

[0052] Figure 4 shows the analysis results. Both the largest variation and normal state value of variation of warpage angles of the medium of Example 1 were smaller than those of the medium of Comparative Example 1. Thus, it is understood that deformation was suppressed in the medium of Example 1. Figure 4 reveals that, according to Example 1, even if the film thickness was 20 μm or less, no significant temporal warpage occurred in response to a temperature change. Further, Figure 4 also shows predicted variations of warpage angles θ calculated in accordance with Equations (1) through (5) above, and these predicted approximate values were very close to the actual values, thereby proving reliability of the approximate values.

[0053] Next, the following will explain a medium (Example 2) using UV curable resin 3 having large Young's modulus. The medium of Example 2 had different UV curable resin characteristics from those in the medium of Example 1. The arrangement of Example 2 is set forth in Table 3 below.

Table 3

Example 2				
	MATERIAL	FILM THICKNESS	YOUNG'S MODULUS (Pa)	LINEAR EXPANSION COEFFICIENT (1/°C)
TRANSPARENT SUBSTRATE	POLYCARBONATE	0.6 mm	2.41E+09	6.00E-05
THIN FILM LAYER	ALUMINUM NITRIDE	79 nm	3.43E+11	5.60E-06
THIN FILM PROTECTING FILM	UV CURABLE RESIN 3	16 μm	3.60E+09	5.68E-05

[0054] A variation of warpage angles θ predicted by calculations in accordance with Equations (1) through (5) above was 5.18 mrad, and it is understood that warpage caused by a temperature change was reduced significantly compared with Comparative Example 1.

[0055] As has been discussed, according to the optical information recording medium of the present embodiment,

temporal significant warpage caused by a temperature change can be suppressed. Thus, even when the temperature of the medium rises while information is recorded or reproduced, problems, such as defective reproduction, can be controlled. In addition, the thin film protecting film 50 can be made thinner.

(Embodiment 2)

[0056] The present embodiment will explain an optical information recording medium which can prevent deformation caused by a humidity change.

① Principle

[0057] The optical information recording medium 10 of Figure 1 employs the substrate made of polycarbonate or the like as the transparent substrate 20. Thus, under high humidity circumstances, the transparent substrate 20 absorbs moisture and expands, thereby causing deformation of the optical information recording medium 10. In particular, when a moisture permeation degree of the substrate protecting film 30 is greater than that of the thin film protecting film 50, a deformation rate of the substrate 20 becomes faster than that of the thin film protecting film 50. Accordingly, large overshoot of a variation occurs when humidity actually changes, thereby raising a serious problem.

[0058] In the present embodiment, the above problem occurring in practical use is solved by suppressing the overshoot by making a moisture permeation degree of the substrate protecting film 30 smaller than that of the thin film protecting film 50.

② Example

[0059] A medium formed as Example 3 was identical with the medium of Example 1 above except that the substrate protecting film 30 made of UV curable resin 4 was additionally provided. A medium formed as Comparative Example 2 for purpose of comparison was also identical with the medium of Example 1 except that the substrate protecting film 30 made of UV curable resin 5 was additionally provided. Moisture permeation degrees of the UV curable resins of Example 3 and Comparative Example 2 are set forth in Table 4 below.

Table 4

	SUBSTRATE PROTECTING FILM		THIN FILM PROTECTING FILM	
	FILM	MOISTURE PERMEATION DEGREE ($g/m^2 \cdot day$)	FILM	MOISTURE PERMEATION DEGREE ($g/m^2 \cdot day$)
EXAMPLE 3	UV CURABLE RESIN 4	2.20E+02	US CURABLE RESIN 1	4.60E+02
COMPARATIVE EXAMPLE 2	UV CURABLE RESIN 5	9.70E+02	UV CURABLE RESIN 1	4.60E+02

[0060] A humidity change was given to the media of Example 3 and Comparative Example 2 (ambient humidity was increased from 50% to 90%), and a variation of warpage angles θ at the outer circumference portion (r=56 mm) with time was analyzed.

[0061] Figure 5 shows the analysis result. The largest variation (at the overshoot) of warpage angles in Example 3 was quite small compared with that in Comparative Example 2, and it is understood that deformation caused by a humidity change was suppressed in the medium of Example 3.

[0062] The foregoing principles stand up for polycarbonate substrates or the like thinner than those used in Examples 1 through 3, which will be explained in Example 4 as follows.

[0063] A medium formed as Example 4 was identical with the medium of Example 3 except that the thickness of the substrate (transparent substrate) 20 was 0.5 mm (the arrangements are set forth in Table 5 below), and a variation of warpage angles θ in response to the temperature change and humidity change was analyzed.

Table 5

	MATERIAL	FILM THICKNESS	YOUNG'S MODULUS (Pa)	LINEAR EXPANSION COEFFICIENT (1/°C)	MOISTURE PERMEATION DEGREE ($g/m^2 \cdot day$)
SUBSTRATE PROTECTION FILM	UV CURABLE RESIN 6	3 μm	6.8E+09	5.0E-05	2.2E+02
TRANSPARENT SUBSTRATE	POLYCARBONATE	0.5 MM	3.3E+09	6.0E-05	
THIN FILM LAYER	ALUMINUM NITRIDE	79 nm	3.4E+11	5.6E-06	
THIN FILM PROTECTING FILM	UV CURABLE RESIN 7	12 μm	5.9E+09	7.2E-05	4.6E+02

[0064] Figures 10 and 11 show the analysis results. Figure 10 shows a transitional variation of tilt along radius in response to a temperature Change (a change from 25°C at 50% to 70°C at 30% was given), and Figure 11 shows a variation of tilt along radius in response to a humidity change (a change from 25°C at 60% to 25°C at 90% was given). The transparent substrate 20 had a minor diameter of 7 mm and a major diameter of 50 mm. The analysis results reveal that the foregoing principles stand up even in a case where a thinner transparent substrate 20 is used, and therefore, a variation of warpage can be also suppressed in such a case.

[0065] As has been discussed, according to the optical information recording medium of the present embodiment, even if humidity changes, no temporal significant warpage occurs, thereby suppressing a problematic defective reproduction when information is recorded and reproduced.

[0066] In the optical information recording medium of the present embodiment, if the physical properties of the thin film protecting film 50 and substrate protecting film 30 are set so as to form the neutral plane of deformation caused by a temperature change within (or in the vicinity of) the thin film layer 40 as was discussed in Embodiment 1, not only can deformation caused by a humidity change be prevented as was discussed herein, but also deformation caused by a temperature change can be prevented.

[0067] As has been discussed, in the present invention, by arranging the optical information recording medium in such a manner that the neutral plane of deformation caused by a temperature change is present within (or in the vicinity of) the thin film layer, such as a magnetic film, a variation caused by a temperature change can be reduced, thereby enhancing information recording and reproducing reliability.

[0068] Also, in the optical information recording medium, by making at least one of Young's modulus and linear expansion coefficient of the thin film protecting film larger than those of the transparent substrate, the thin film protecting film can be made thinner. Consequently, the optical information recording medium can be readily manufactured. Moreover, in case of a magneto-optical recording medium, the magnetic characteristics can be improved.

[0069] In addition, by providing a substrate protecting film having a smaller moisture permeation degree than that of the thin film protecting film, a variation caused by a humidity change can be reduced, thereby enhancing information recording and reproducing reliability.

[0070] An optical information recording medium of the present invention, including at least a transparent substrate, a thin film layer formed on the transparent substrate and having at least one of a recording film and a reflecting film, and a thin film protecting film formed on the thin film layer and mainly made of resin, may be arranged in such a manner that the neutral plane of deformation in the film thickness direction caused by a temperature change while information is recorded and reproduced is present in the vicinity of the thin film layer.

[0071] Also, an optical information recording medium of the present invention, including at least a transparent substrate, a thin film layer formed on the transparent substrate and having at least one of a recording film and a reflecting film, and a thin film protecting film formed on the thin film layer and mainly made of resin, may be arranged in such a manner that bending moments applied on the thin film layer from the both sides in the film thickness direction are substantially equal.

[0072] In addition, an optical information recording medium of the present invention, including at least a transparent

substrate, a thin film layer formed on the transparent substrate and having at least one of a recording film and a reflecting film, and a thin film protecting film formed on the thin film layer and mainly made of resin, may be arranged in such a manner that at least one of Young's modulus and the linear expansion coefficient of the thin film protecting film is larger than those of the transparent substrate, respectively.

[0073] Further, an optical information recording medium of the present invention may be arranged in such a manner that the film thickness of the thin film protecting film is 20 μm or less.

[0074] In addition, an optical information recording medium of the present invention, including at least a transparent substrate, a thin film layer formed on the transparent substrate and having at least one of a recording film and a reflecting film, a thin film protecting film formed on the thin film layer and mainly made of resin, and a substrate protecting film formed on the light incident side of the transparent substrate and mainly made of resin, may be arranged in such a manner that a moisture permeation degree of the thin film protecting film is smaller than that of the substrate protecting film.

[0075] The neutral plane of deformation referred to herein means a plane expressed by a value of y when warpage angles θ is almost 0 (zero) in Equations (1) through (5) above.

[0076] The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

Claims

1. An optical information recording medium including:

   a thin film layer (40), formed on a substrate (20), for recording and reproducing information; and
   a thin film protecting film (50), formed on said thin film layer (40), for protecting said thin film layer (40),
   a neutral plane of deformation in a thickness direction caused by a temperature change being present in a vicinity of said thin film layer (40).

2. An optical information recording medium including:

   a thin film layer (40), formed on a substrate (20), for recording and reproducing information; and
   a thin film protecting film (50), formed on said thin film layer (40), for protecting said thin film layer (40),
   bending moments applied on said thin film layer (40) from a substrate (20) side and a thin film protecting film (50) side in response to a temperature change being substantially cancelled out with each other.

3. The optical information recording medium of Claim 1, wherein a thickness, Young's modulus, and a linear expansion coefficient are set to their respective desired values in each of said substrate (20), thin film layer (40), and thin film protecting film (50), so that the neutral plane of deformation in the thickness direction caused by a temperature change is present in the vicinity of said thin film layer (40).

4. The optical information recording medium of Claim 3, wherein at least one of Young's modulus and the linear expansion coefficient of said thin film protecting film (50) is larger than one of Young's modulus and the liner expansion coefficient of said substrate (20), respectively.

5. The optical information recording medium of Claim 3, wherein the thickness of said thin film protecting film (50) is 20 μm or less.

6. The optical information recording medium of Claim 1, further including a substrate protecting film (30), formed on said substrate (20) on a surface opposite to a surface where said thin film layer (40) is formed, for protecting said substrate (20), a moisture permeation degree of said substrate protecting film (30) being smaller than a moisture permeation degree of said thin film protecting film (50).

7. An optical information recording medium including:

   a thin film layer (40), formed on a substrate (20), for recording and reproducing information;
   a thin film protecting film (50), formed on said thin film layer (40), for protecting said thin film layer (40); and
   a substrate protecting film (30), formed on said substrate (20) on a surface opposite to a surface where said thin film layer (40) is formed, for protecting said substrate (20),
   a moisture permeation degree of said substrate protecting film (30) being smaller than a moisture permeation degree of said thin film protecting film (50).

8. An optical information recording medium at least including:

a transparent substrate (20);
a thin film layer (40) formed on said transparent substrate (20) and having at least one of a recording film (42) and a reflecting film (44); and
a thin film protecting film (50) formed on said thin film layer (40) and mainly made of resin,
a neutral plane of deformation in a film thickness direction caused by a temperature change while information is recorded and reproduced being present in a vicinity of said thin film layer (40).

9. An optical information recording medium at least including:

a transparent substrate (20);
a thin film layer (40) formed on said transparent substrate (20) and having at least one of a recording film (42) and a reflecting film (44); and
a thin film protecting film (50) formed on said thin film layer (40) and mainly made of resin,
bending moments applied on said thin film layer (40) from both sides thereof in a film thickness direction being substantially equal.

10. An optical information recording medium at least including:

a transparent substrate (20);
a thin film layer (40) formed on said transparent substrate (20) and having at least one of a recording film (42) and a reflecting film (44); and
a thin film protecting film (50) formed on said thin film layer (40) and mainly made of resin,
at least one of Young's modulus and a linear expansion coefficient of said thin film protecting film (50) being larger than one of Young's modulus and a liner expansion coefficient of said transparent substrate (20), respectively.

11. The optical information recording medium of Claim 8, 9, or 10, wherein a film thickness of said thin film protecting film (50) is 20 μm or less.

12. An optical information recording medium at least including:

a transparent substrate (20);
a thin film layer (40) formed on said transparent substrate (20) and having at least one of a recording film (42) and a reflecting film (44);
a thin film protecting film (50) formed on said thin film layer (40) and mainly made of resin; and
a substrate protecting film (30) formed on a light incident side of said transparent substrate (20) and mainly made of resin,
a moisture permeation degree of said substrate protecting film (30) is smaller than a moisture permeation degree of said thin film protecting film (50).

FIG. 1

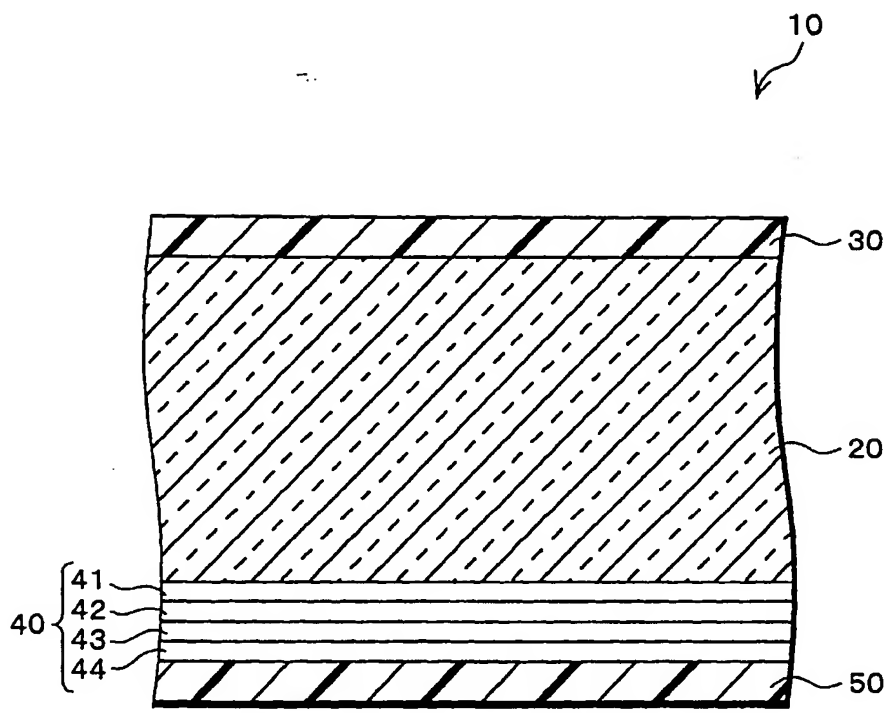


FIG. 2 (a)

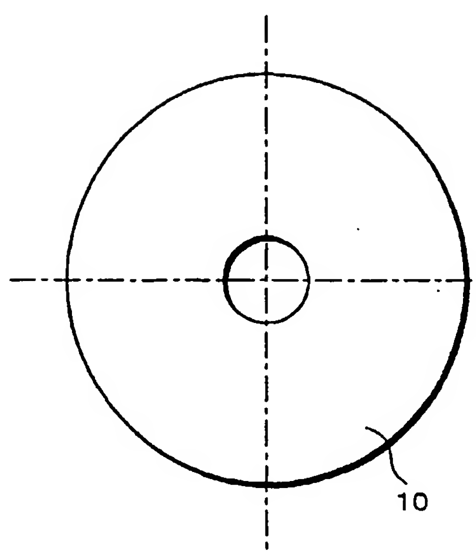

10

FIG. 2 (b)

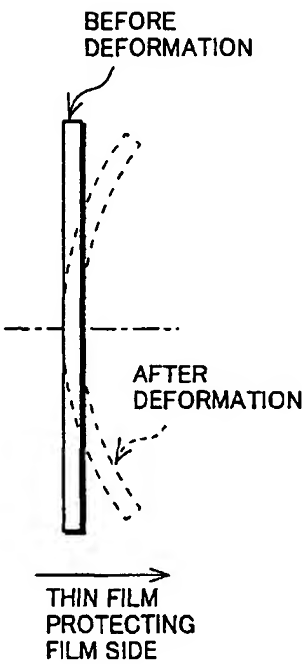

BEFORE DEFORMATION
AFTER DEFORMATION
THIN FILM PROTECTING FILM SIDE

FIG. 3

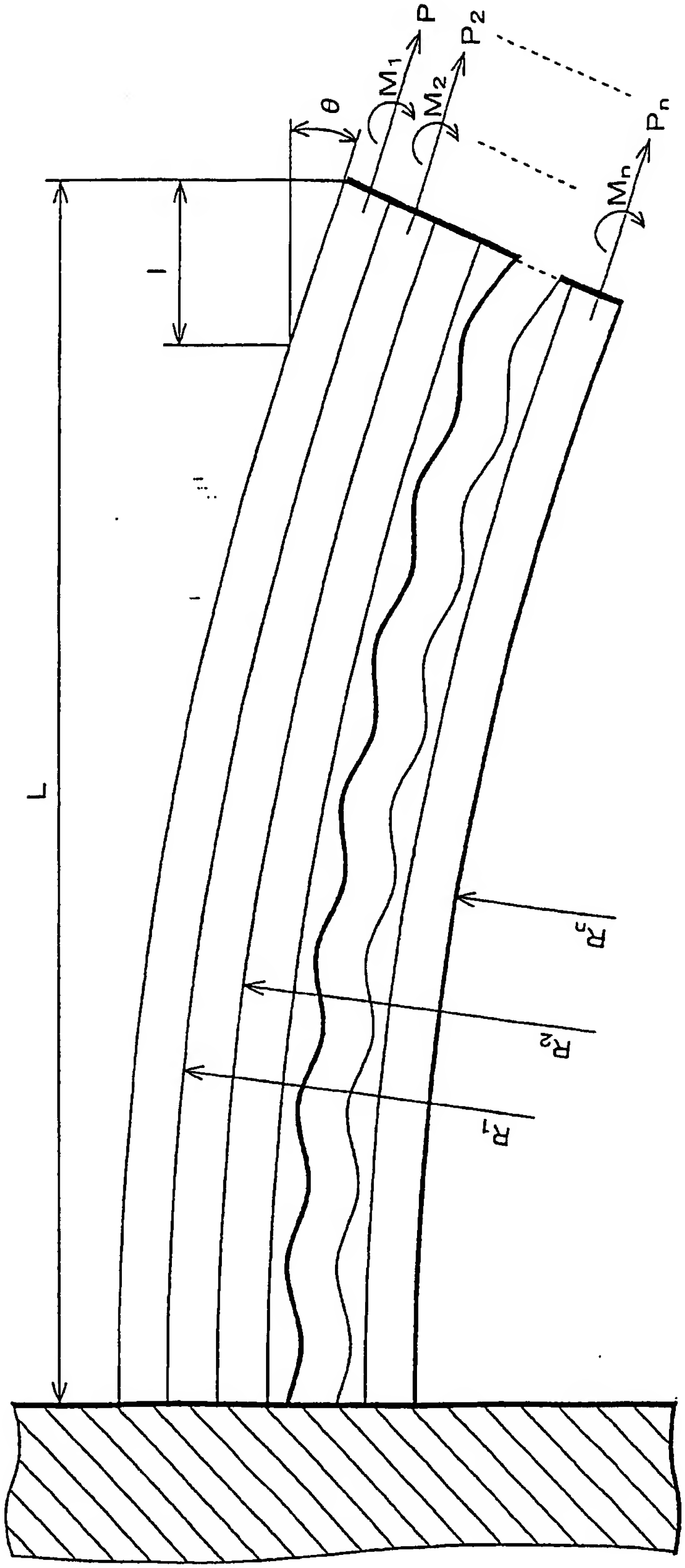


FIG. 4

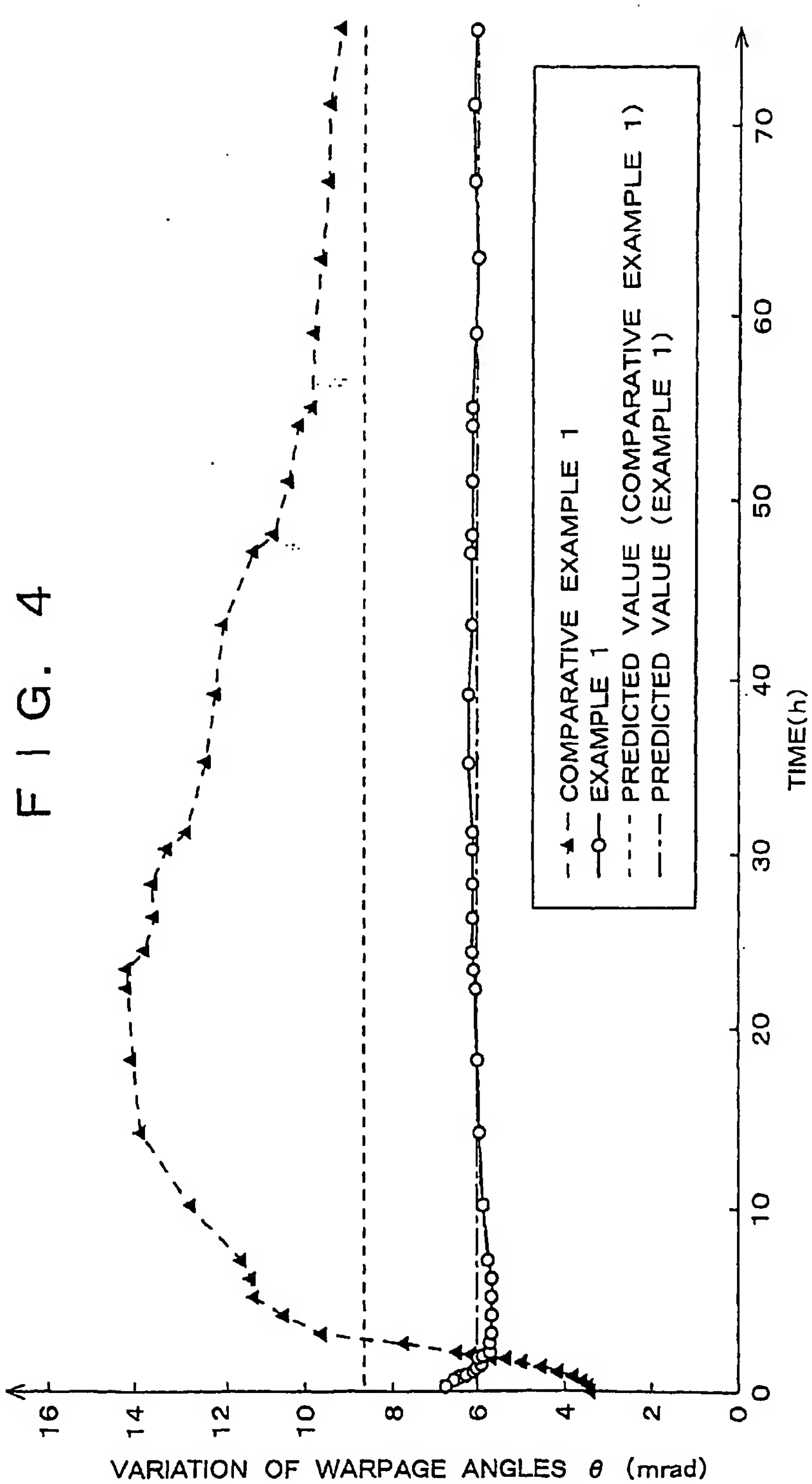
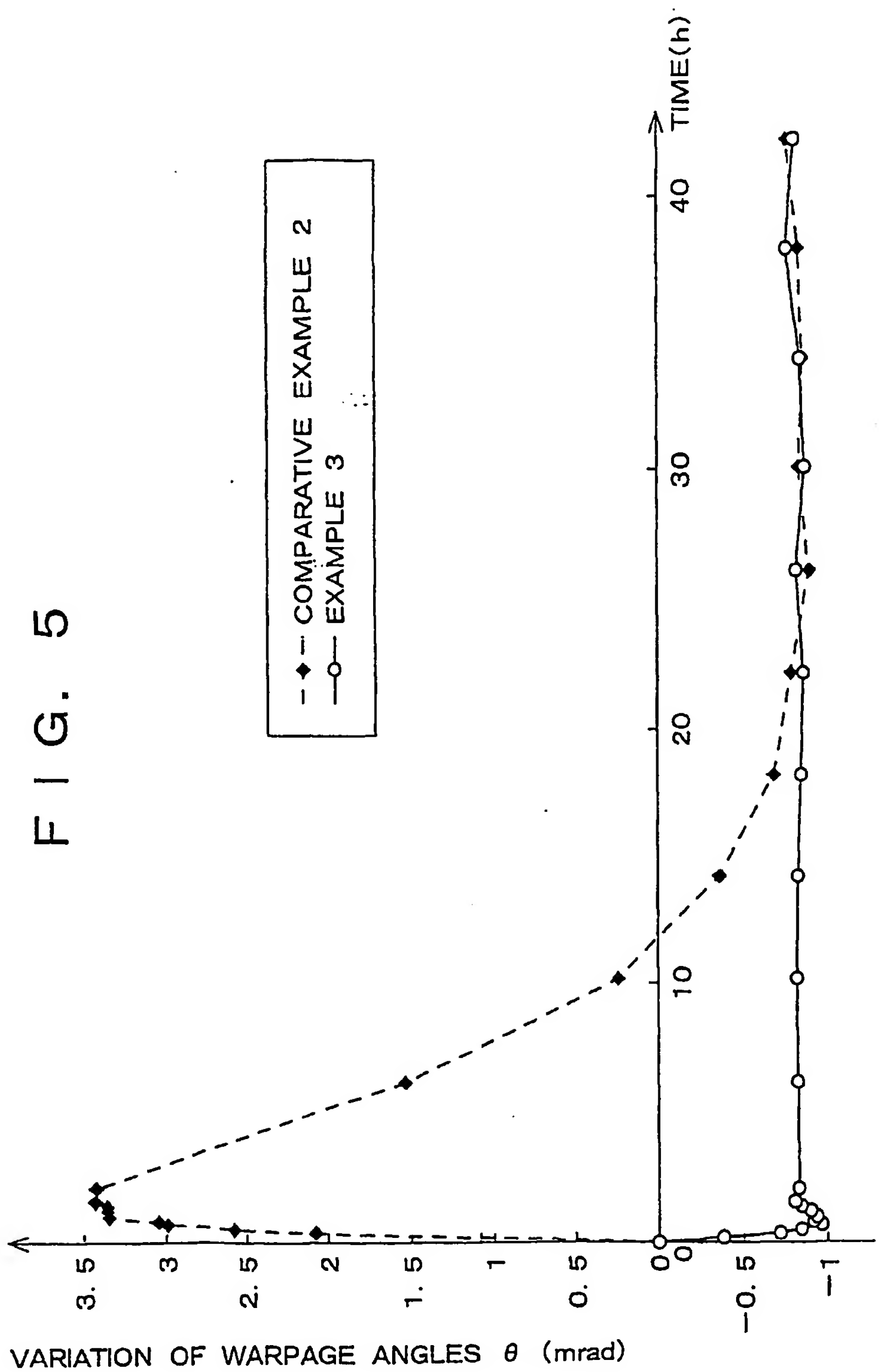
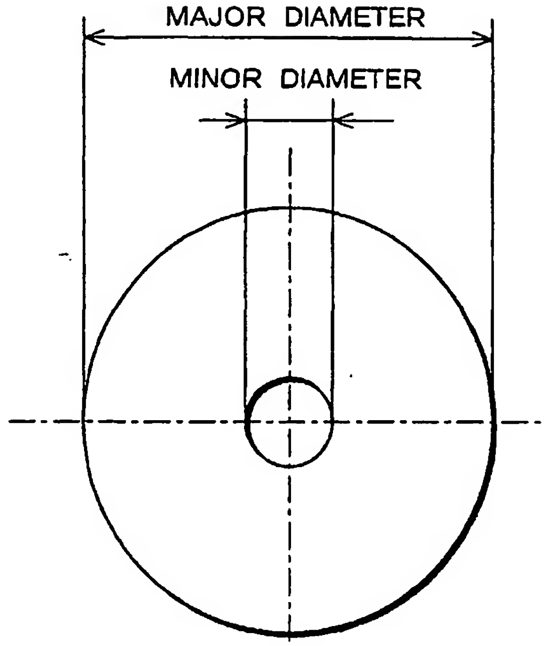

COMPARATIVE EXAMPLE 1
EXAMPLE 1
PREDICTED VALUE (COMPARATIVE EXAMPLE 1)
PREDICTED VALUE (EXAMPLE 1)
VARIATION OF WARPAGE ANGLES θ (mrad)
TIME(h)
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50
60
70

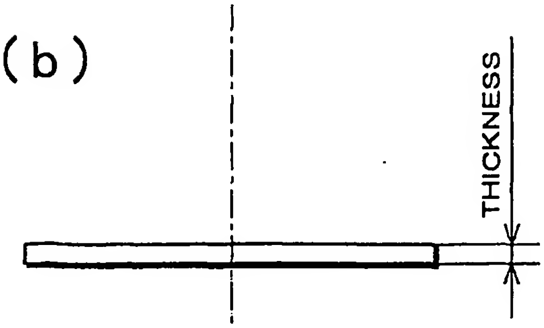
FIG. 5


COMPARATIVE EXAMPLE 2
EXAMPLE 3
TIME(h)
10
20
30
40
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-1
VARIATION OF WARPAGE ANGLES θ (mrad)

F I G. 6 (a)



F I G. 6 (b)



F I G. 7

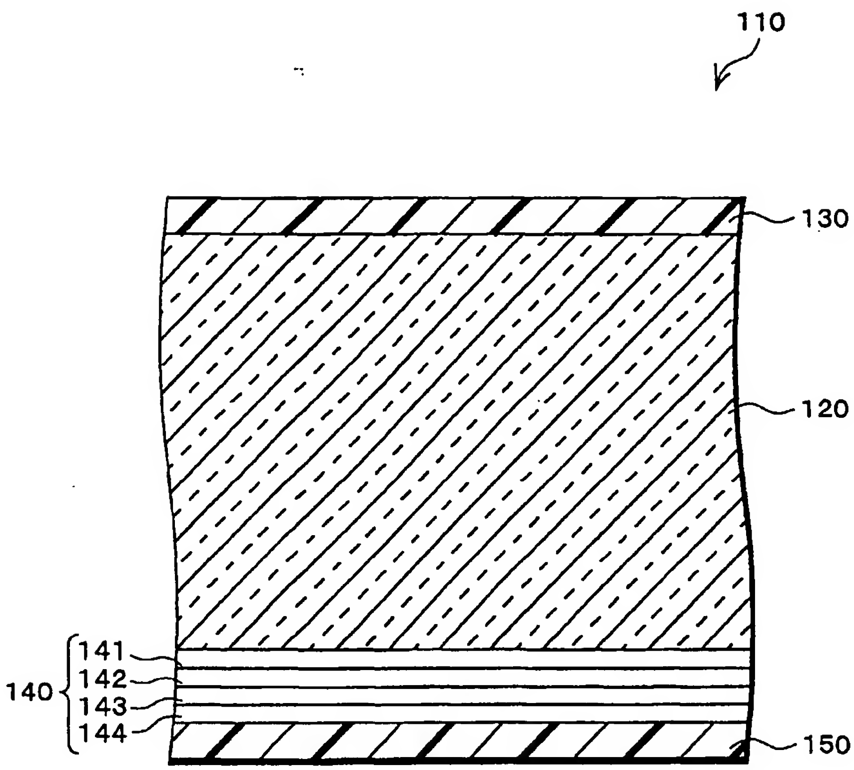


FIG. 8

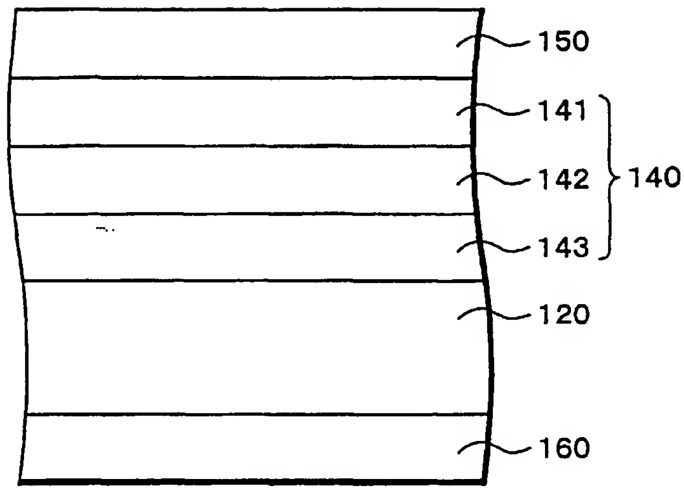


FIG. 9

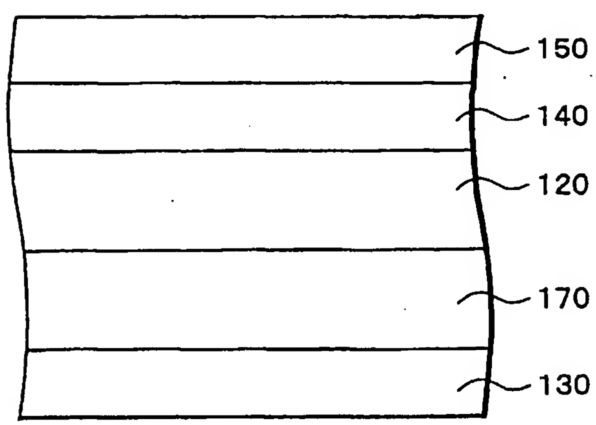


FIG. 10

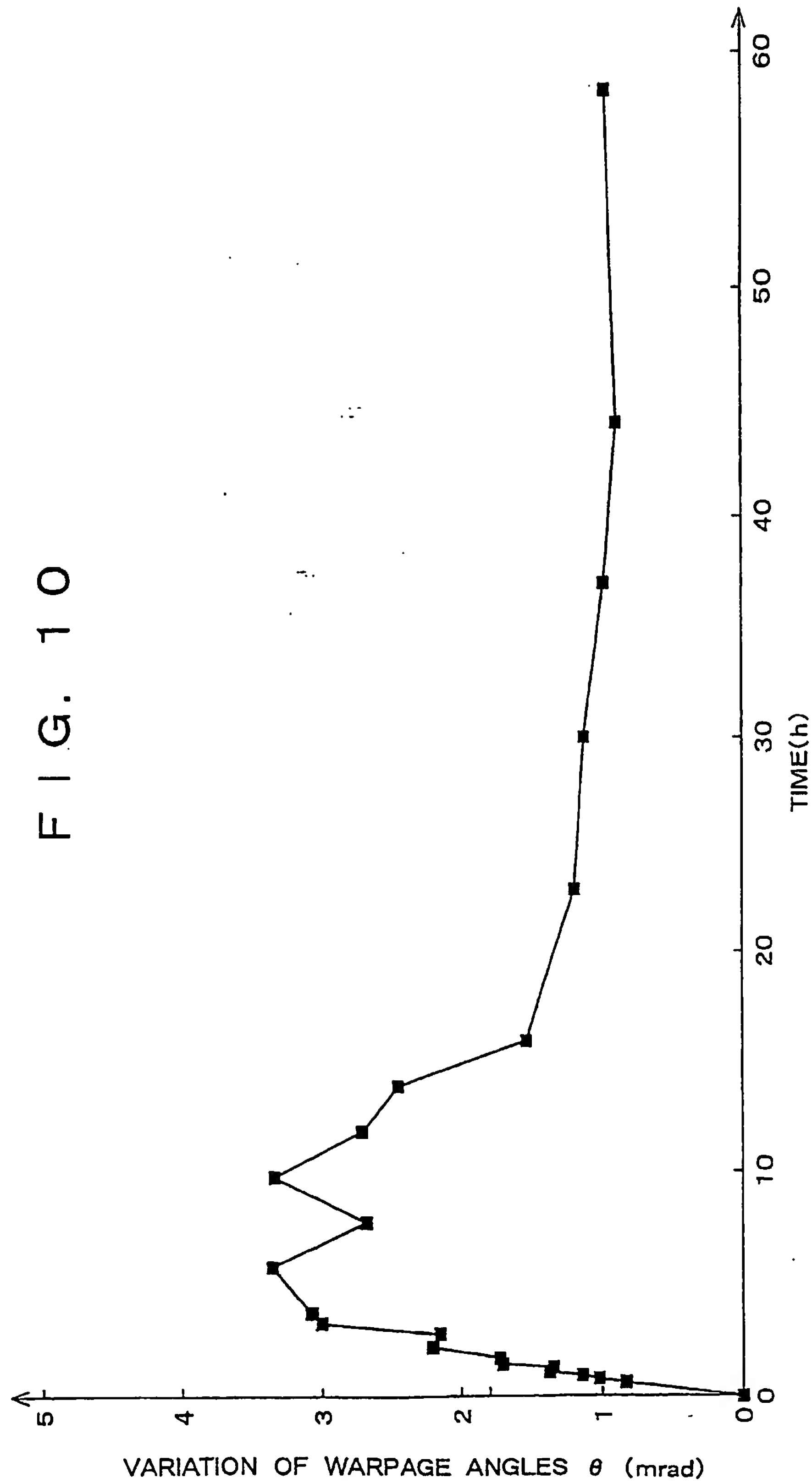
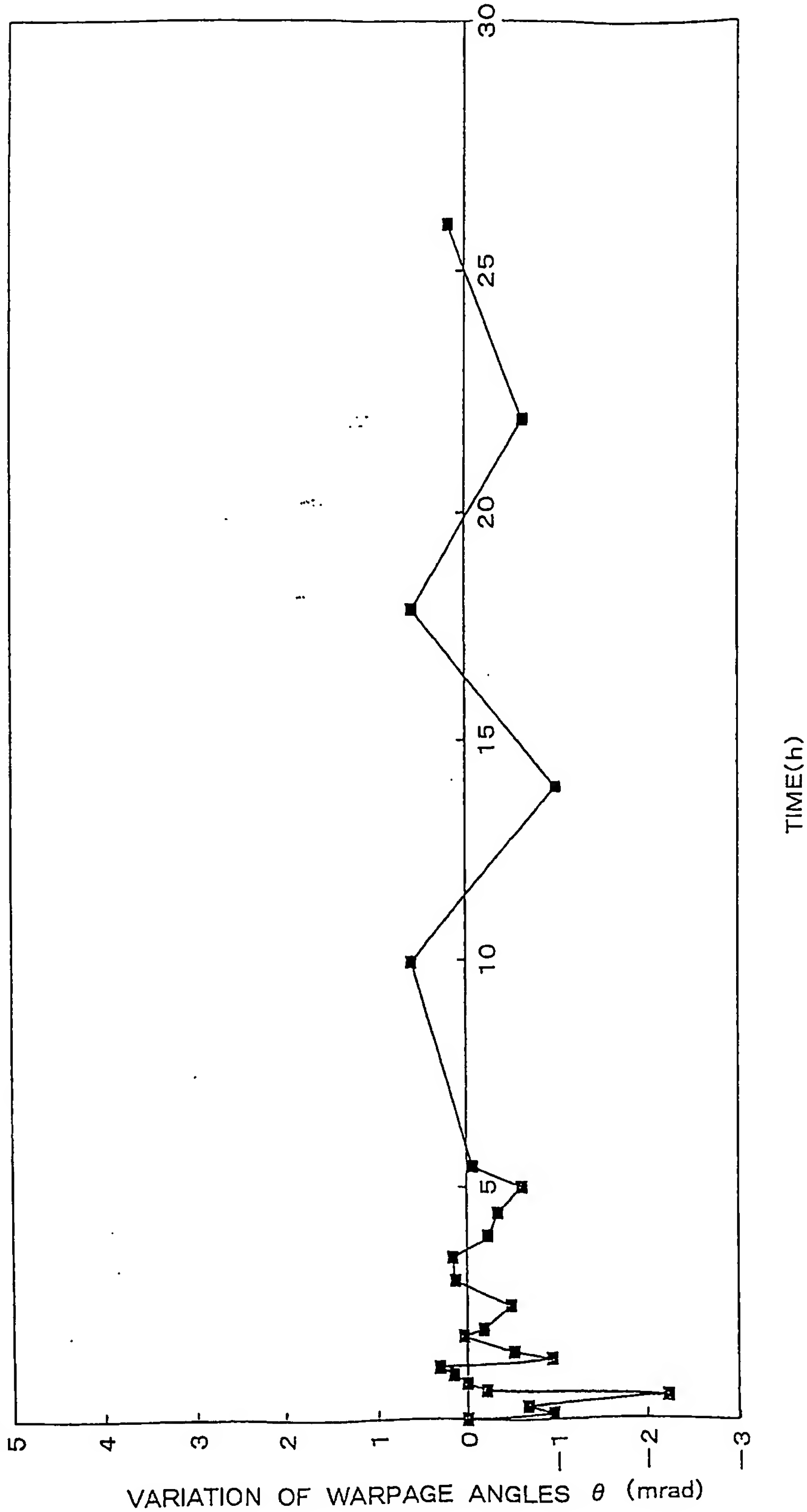

VARIATION OF WARPAGE ANGLES θ (mrad)
TIME(h)
0
1
2
3
4
5
10
20
30
40
50
60

FIG. 11


VARIATION OF WARPAGE ANGLES θ (mrad)
5
4
3
2
1
0
−1
−2
−3
TIME(h)
5
10
15
20
25
30

Appendix E

Murakami neither discloses nor suggests imposing such a performance requirement on the materials used for the optical recording medium recited therein. Moreover, no extrinsic evidence has been presented to show or establish that the protective layers or transparent substrates of the optical recording media of Murakami <u>necessarily possess</u> the linear expansion coefficients recited in claims 10 and 14, as currently amended.

Applicants respectfully submit that the materials disclosed in the Murakami reference do not <u>necessarily possess</u> the properties of the claimed invention. Materials described in similar general terms can and often do have quite different properties, including different linear expansion coefficients. For example, as shown on the attached Table (Exhibit A), materials generically termed "acrylic UV curable resins" having similar principal components can nevertheless have a range of linear expansion coefficients (in the Table, ranging from about 1.10×10^{-5} to about 1.46×10^{-4} (l/°C) (note that the acrylic ester commercial product listed at the bottom of the Table does not have a linear expansion coefficient within the range required by the instant claims). It is clear that a reference disclosing an acrylic UV curable resin would not <u>necessarily</u> provide a disclosure of an acrylic UV curable resin having a linear expansion coefficient *in a specific range*. So it is with the Murakami reference, which at the portion cited by the Examiner (Column 8, lines 47-49), states that an "overcoat film" can be an "ultraviolet hardening resin from polyurethane acrylate series." This disclosure does not expressly nor inherently describe a protective film having a linear expansion coefficient of the greater than 9.5×10^{-5} (l/°C) and smaller than 5.0×10^{-4} (1/°C), as required by the pending claims. Therefore, the Murakami reference does not and cannot anticipate the pending claims.

For at least the reasons discussed herein, claims 10, 14, and 18 are patentable over the Murakami patent (Applicants note that claims 17-22 were not rejected under 35 U.S.C. §102(b) over Murakami). Claims 11-13, 15-17, and 19-22 depend from claims 10, 14 or 18 and are therefore also patentable over the Murakami patent.

Separate Sheet A

Acrylic UV Curable Resin		Liner Expansion Coefficient of Protective Film (1/K)
Acrylic UV Curable Resin	Principal Components	
A	Mixture of Acrylate Oligomer (Acrylic Ester), Acrylate Monomer, and Photopolymerization Initiator	9.70E-05
B		1.17E-04
C		1.15E-04
D		1.10E-04
E		1.12E-04
F		1.17E-04
G		1.13E-04
H		1.10E-04
I		1.15E-04
J		6.38E-05
K		8.60E-05
L		1.10E-05
M		1.46E-04
Commercial Acrylic UV Curable Resin	Acrylic Ester Compound	6.01E-05

Note: Acrylic UV curable resins A-M are not commercial products, but are test products whose names are not given.

Appendix F

Claims 10-16 were rejected under 35 U.S.C. §102(b) as being allegedly anticipated by Tachibana (U.S. Patent 5,102,709), and claims 10-22 were rejected under 35 U.S.C. §103(a) as being allegedly obvious in view of Tachibana.

The resin composition disclosed in Example 3 of Tachibana (KAYARAD DPCA-30 (70%), KAYARAD R-604 (25%), IRG-184, 5%) has a linear expansion coefficient of 9.0×10^{-5} (1/°C). As the Examiner will appreciate, this linear expansion coefficient is not within the range of values of the linear expansion coefficient recited by the pending claims (greater than 9.5×10^{-5} (1/°C) and smaller than 5.0×10^{-4}(1/°C)). Thus, this composition does not in fact possess the properties of the claimed invention, and cannot anticipate the pending claims. Applicants submit that there is no teaching or suggestion in Tachibana that the this resin or any other materials disclosed therein <u>necessarily possess</u> all the properties recited in the pending claims. Accordingly, the rejection of the pending claims is improper and should be withdrawn.

Reconsideration and allowance of claims 10-22 is respectfully requested in view of the foregoing discussion.

<u>Conclusion</u>

This case is believed to be in condition for immediate allowance. Applicant respectfully requests early consideration and allowance of the subject application.

Although no extension of time is believed to be required, Applicants conditionally petition for any extension of time needed. If for any reason a fee is required, a fee paid is inadequate or credit is owed for any excess fee paid, you are hereby authorized and requested to charge Deposit Account No. **04-1105**.

O I P E IAP17
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Application No. (if known): 10/002,949 Attorney Docket No.: 56702(70801)

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Appeal Brief (32 pages with Exhibits A-F)
Appeal Brief Transmittal (1 page)
One Month Request for Extension of Time Under 37 CFR 1.136(a) (1 page)
Charge $120.00 to deposit account 04-1105